

Research paper

Exceptional energy absorption characteristics and compressive resilience of functional carbon foams scalably and sustainably derived from additively manufactured kraft paper

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ARTICLE INFO

Keywords:

Kraft paper
Glassy carbon
Cellulose
Additive manufacturing
Pyrolysis

ABSTRACT

To incentivize carbon sequestration activities, kraft paper, a renewable and recyclable bioproduct that is already manufactured at scale, is proposed as feedstock for producing economically viable carbon materials. The paper was first additively manufactured into 3D open cell honeycombs and closed cell plate lattices using a sheet lamination process before being pyrolyzed into paper-derived architected carbon foams (PDACFs). In the iso-stress orientation, PDACFs displayed low moduli, high elastic strains (~30–40%) and a compressive resilience similar to graphene aerogels, but at stresses up to ~3 orders of magnitude higher, despite the brittle nature of the carbonized fibers. In the isostrain orientation, PDACFs exhibited better moduli (~1 MPa – 1 GPa), which were comparable to conventional carbon foams, and smaller elastic strains (~5–10%). Failure in isostrain orientation proceeded by fracture propagation through and/or between the layers while cracks in the isostress orientation extended mainly across the layers. The strength of the PDACFs (~0.2 – 14 MPa) was similar in both orientations, however, likely because both interlayer and intralayer failure onset involved microscopic fractures initiating and propagating through a multitude of carbonized fiber interfaces. Notably, Honeycombs and Plate Simple Cubic PDACFs exhibited a combination of strength (> 3 MPa) and energy absorption (> 1 MJ/m³; > 1 kJ/kg) not found in porous carbon materials previously, suggesting that the hierarchical arrangement of carbonized fibers within a macroscopic lattice architecture is better for dissipating energy than the tetrakaidecahedron microstructure commonly found in foams. Furthermore, as an electrode in a Li-ion battery, the carbonized cellulose making up PDACFs showed reversible specific capacities of 65–140 mAh/g at a specific current of 10 mA/g for 300 cycles, which is comparable to that of commercial lithium manganese oxide batteries and graphitic anodes derived from non-renewable polymer foams.

1. Introduction

As climate change intensifies and manifests itself in the form of record-setting natural disasters such as heatwaves, droughts and floods in recent years, there is a major impetus to reduce the greenhouse gases in the atmosphere [1,2]. Nature contributes to this goal by converting carbon dioxide into biomass and sequestering 40 – 250 million tons of carbon in the soil and water bodies through forest fires every year [3]. This alone, however, is insufficient to avert climate change [4]. Therefore, to accelerate the rate of greenhouse gas removal, efforts have been

directed towards improving the financial incentive for carbon capture and sequestration activities [5]. One strategy is to process captured carbon into economically viable structural materials, such as carbonate fillers in concrete [6], carbon fibers from lignin [7,8] and polymers such as polyurethane [9,10]. Porous carbon materials are a promising option as well, as they are typically demanded in relatively large volumes for a variety of high value applications, such as electrochemical storage in supercapacitors and batteries [11,12], electromagnetic shielding [13], aqueous-organic solvent separation [14,15] and thermal barriers for aerospace vehicles [16,17].

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<https://doi.org/10.1016/j.addma.2022.102992>

Received 5 March 2022; Received in revised form 8 June 2022; Accepted 21 June 2022

Available online 26 June 2022

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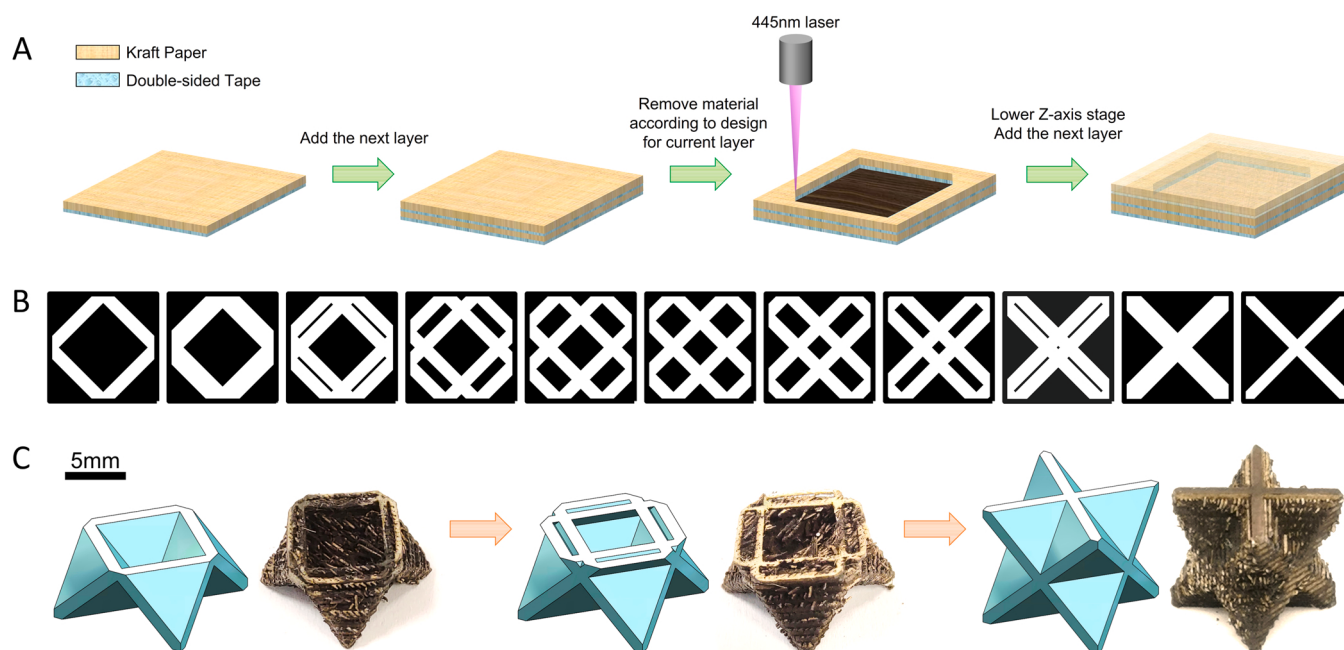


Fig. 1. (A) Schematic diagram illustrating the additive manufacturing of PDACF (Paper-Derived Architected Carbon Foams) via the ERASL (ERadication of Area in Sheet Lamination) technique. The topmost layer is rendered translucent to reveal the closed cell cavity in the structure. (B) The distinct designs for each layer in a single unit cell of Plate Octet Truss structure. The parts to be removed by the laser are in black. (C) Comparison between the 3D CAD model and actual kraft paper Plate Octet Truss structure at various stages of the fabrication.

Current processing techniques for porous carbon materials can mainly be categorized into bottom-up and top-down approaches. In the bottom-up approach, carbon aerogels can be fabricated by growing carbon films on porous templates through chemical vapor deposition (CVD) and then removing the templates with an etchant and supercritical drying [11,18–20]. Alternatively, they can also be synthesized through the self-assembly of emulsified nano-carbon (e.g. graphene platelets, carbon nanotubes *etc.*) using freeze drying [15,21] or supercritical drying. These processes produce extremely lightweight and porous carbon aerogels that typically exhibit large elastic recoveries (*i.e.* high compressive resilience) and excellent energy absorption efficiencies (*i.e.* cushioning properties) that are desirable for impact resistant devices [22–25].

However, the modulus, strength and volumetric energy absorption of these materials are fairly low ($\leq$ kPa and kJ/m^3) compared to existing structural materials and thus, they are unsuitable for most load bearing and shock absorption applications. While carbon micro-/ nano- lattices with extremely high modulus and strength have been demonstrated in recent years [26–29], the techniques involved cannot be scaled up to produce sample sizes beyond millimeter dimensions. Even for carbon aerogel production, mass manufacturing is somewhat limited by the long durations (~ 1 week) of solvent exchange procedures [19,21] and high cost of processes such as CVD and supercritical drying.

In contrast, techniques employed in the top-down approach are usually highly scalable. The process typically begins with the introduction of air pores to a polymer resin through mechanical means [30] or the addition of blowing agents [31]. The resultant polymer foams are then pyrolyzed into carbon foams in an inert atmosphere. The mass density of carbon foams obtained this way ($\geq 50 \text{ mg/cm}^3$) tend to be higher than carbon aerogels and thus, their modulus, strength and volumetric energy absorption are correspondingly greater – up to MPa and MJ/m^3 . However, foam failure tends to occur through brittle fracture, leading to poor compressive resilience and energy absorption efficiencies.

Moreover, top-down production techniques generally do not contribute to carbon sequestration – the majority of the current methods rely on the use of non-renewable fossil fuels such as pitch and coal tar

[32,33] or highly toxic polymers such as phenolic and melamine resins as carbon sources [17,30]. While there have been a few studies that reported the production of carbon foams using bread [13], winter melon [14] and watermelon [34], these sources are not encouraged, as the increased competition for edible feedstock will lead to the expansion of farms, which is a leading cause of deforestation [35], thus setting back carbon sequestration efforts.

Therefore, to address these ecological, scalability and performance deficits in current carbon aerogels and foams, we propose to use kraft paper as the raw material for the pyrolytic production of a novel form of porous carbon material. Unlike carbon aerogels and foams that typically exhibit a cellular microstructure [15,20,21,31], kraft paper porosity arises from the loose packing of long cellulosic fibers derived from renewable non-food-based bioresources *e.g.* softwood pulp [36]. This microstructure, when assembled into macroscopic lattices through additive manufacturing, confers a unique, hierarchical porosity to the Paper-Derived Architected Carbon Foams (PDACF) after pyrolysis. Adding to its appeal, kraft paper can also be cheaply mass produced, with the potential of becoming a negative CO_2 emissions product [37]. Although pyrolysis of cellulose had previously been investigated for the formation of biochar [38], biofuel [39] and carbon fibers [40], the mechanical properties of carbonized kraft paper, to the best of our knowledge, have yet to be systematically investigated and forms the main aim of the present study.

2. Materials and methods

2.1. Additive manufacturing of paper-derived architected carbon foams (PDACF)

Sheet lamination was employed to additively manufacture 3D structures of kraft paper before carbonization, as the technique has been shown to work well with cellulose paper. A 0.5 mm thick, 350 gsm kraft paper (DAISO, Singapore) was first laid over the preceding layer by means of an acrylic adhesive tape that was ~ 0.1 mm thick (467 MP, 3 M Singapore) (Fig. 1 A). Unfortunately, the average length of individual kraft fibers could not be reliably traced and quantified with microscopy

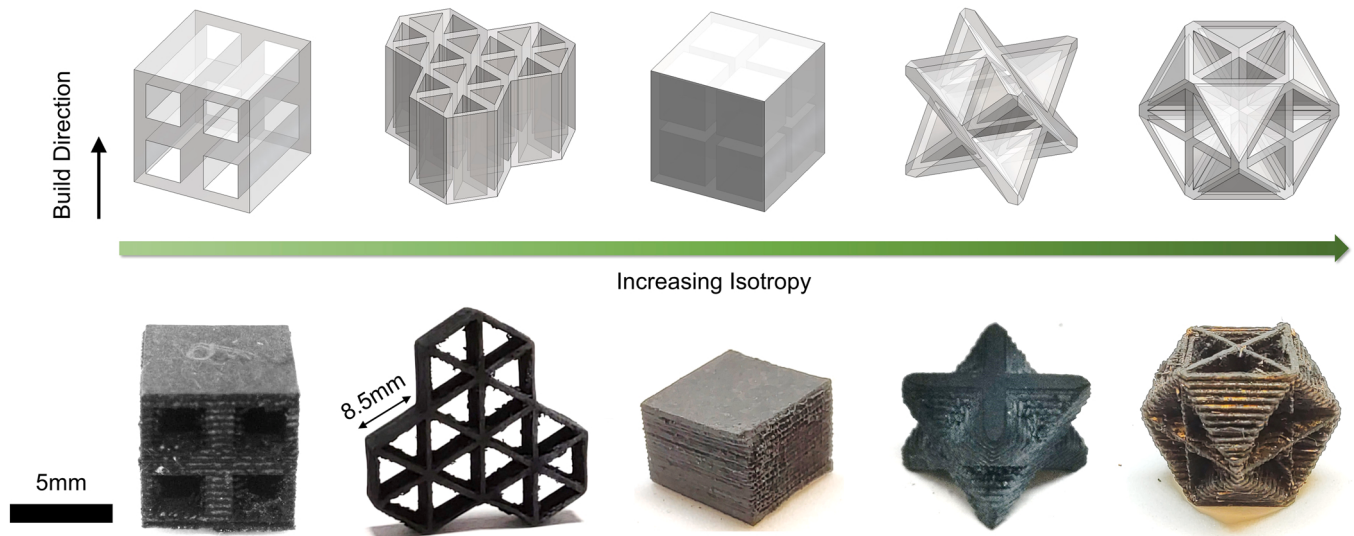


Fig. 2. (top) CAD and (bottom) PDACF structures of (left to right) Square Honeycomb (Square HC), Triangle Honeycomb (Triangle HC), Plate Simple Cubic (Plate SC), Plate Octet Truss (Plate OT) and Plate Simple Cubic - Octet Truss (Plate SC-OT) geometries. The CAD models are made translucent to reveal the voids in the structures. Scale bar is applicable to all PDACF structures except for Triangle HC.

due to the chaotic nature of the fiber arrangements, and the use of chemical and/ or mechanical agitation to isolate the fibers would risk altering their length.

Next, a 5 W, 445 nm laser with a focused spot size of $0.23 \text{ mm} \times 0.23 \text{ mm}$ (AtomStack A5 Pro, AtomStack Technologies Co. Ltd) was used to remove unwanted regions according to the pattern input for that layer. The laser power and scan speed were optimized to cut through only 1 layer of kraft paper, so that each layer in the build can be patterned independently. The practical x-y resolution of the laser cutting process was 0.5 mm while the z-axis resolution was limited by the sheet thickness which was 0.5 mm in this study. The patterns for each layer were obtained by slicing the STL file of the desired geometry using a custom MATLAB code (Fig. 1B). The STL files were generated using Solidworks 2020 (Dassault Systemes).

Lastly, the build, which was mounted on a movable stage, was lowered by the thickness of a taped paper sheet and the next layer was added. This step ensured that the distance between the laser and each new paper sheet was constant, so the cutting parameters would be the same for each layer in the build. The processes were then repeated until the structure was completed (Fig. 1 C). Pyrolysis of the part was then carried out at a maximum temperature of 1200°C in Ar to produce Paper-Derived Architected Carbon Foams (PDACF) (Appendix A1).

Unlike traditional sheet lamination techniques, such as Laminated Object Manufacturing [41], which simply cut the outline and crosshatch unwanted areas for waste disposal during post-print processing, our fabrication route involves burning off the entire unwanted area using the laser. To emphasize this difference, we will refer to our approach as ERASL (ERadication of Area in Sheet Lamination) from here on.

2.2. Materials characterization

Helium gas pycnometry was conducted using Ultracp 5000 (Anton Parr, Germany). Scanning Electron Microscopy was performed using JSM-7600 F (JEOL Inc., Japan) at an accelerating voltage of 15 – 20 kV. X-ray diffraction was conducted using a Panalytical X'Pert Pro X-ray diffractometer (Malvern Panalytical Ltd, United Kingdom) with Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$) at a power of 40 kV and 30 mA. Raman Spectroscopy was carried out using an optical microscope (Leica DM 2500 M) coupled with a Renishaw He-Ne laser ($\lambda = 633 \text{ nm}$) as the excitation source.

2.3. Mechanical characterization

Quasistatic compression of samples was performed at a strain rate of $\sim 0.01/\text{s}$ and a minimum acquisition rate of 100 Hz using Shimadzu Autograph AGS-X and AG-500A (Shimadzu Corporation, Japan) fitted with 10 kN and 50 kN load cells respectively.

2.4. Battery cycling tests

For battery cycling tests, carbonized kraft paper and a composite composed of carbonized kraft paper and carbonized acrylic tape were separately assembled with Li metal as a counter electrode into a 2032 coin cell setup in an Ar-filled glove box. Celgard 2325 was used as a separator. The electrolyte was 1 M LiPF₆ in EC/DEC/DMC (4/3/3 by volume). Galvanostatic charge and discharge (0.01–3 V) tests were performed on Battery Testing Equipment (Neware Electronic Co., China) at ambient temperature.

2.5. Finite element simulations

Finite element analysis simulations were performed using Abaqus, with the 'Dynamic, Implicit' solver under 'quasistatic' and 'non-linear geometry' settings. The CAD models were meshed with either hexahedron C3D8R or tetrahedron C3D10 elements. Typical element sizes were 1/3 of the plate thicknesses or smaller to ensure good mesh convergence.

Assuming that the layers in PDACFs were stacked along the z axis and since the cellulose fibers were randomly aligned along the x-y plane in each layer, the PDACF composite can be modeled as a transversely isotropic material i.e. $E_x = E_y \neq E_z$, $G_{xy} = E_x/[2(1 + \nu)]$ and $G_{xz} = G_{yz} \neq G_{xy}$. The linear elastic Young's moduli was experimentally determined to be $E_x = E_y = 580 \text{ MPa}$ and $E_z = 38.2 \text{ MPa}$, while the plastic yield stress was assigned as 12.4 MPa, with perfect plastic hardening, in the x, y and z axes. The failure stress was modeled as isotropic since the empirical values happened to be similar in all the axes (to be presented in Results section). The Poisson's ratio, ν , was assumed to be 0.2 and uniform across all xy, yz, and xz orientations, while G_{xz} was assumed to be equivalent to $(E_z/E_x) \cdot (G_{xy})$.

For each lattice geometry, one face was displaced inwards with an effective strain rate of 0.01/s to simulate the quasistatic uniaxial compression. The corresponding reaction force on the face was then measured and converted into engineering stress-strain curves by normalizing against the lattice dimensions. The linear slope of the

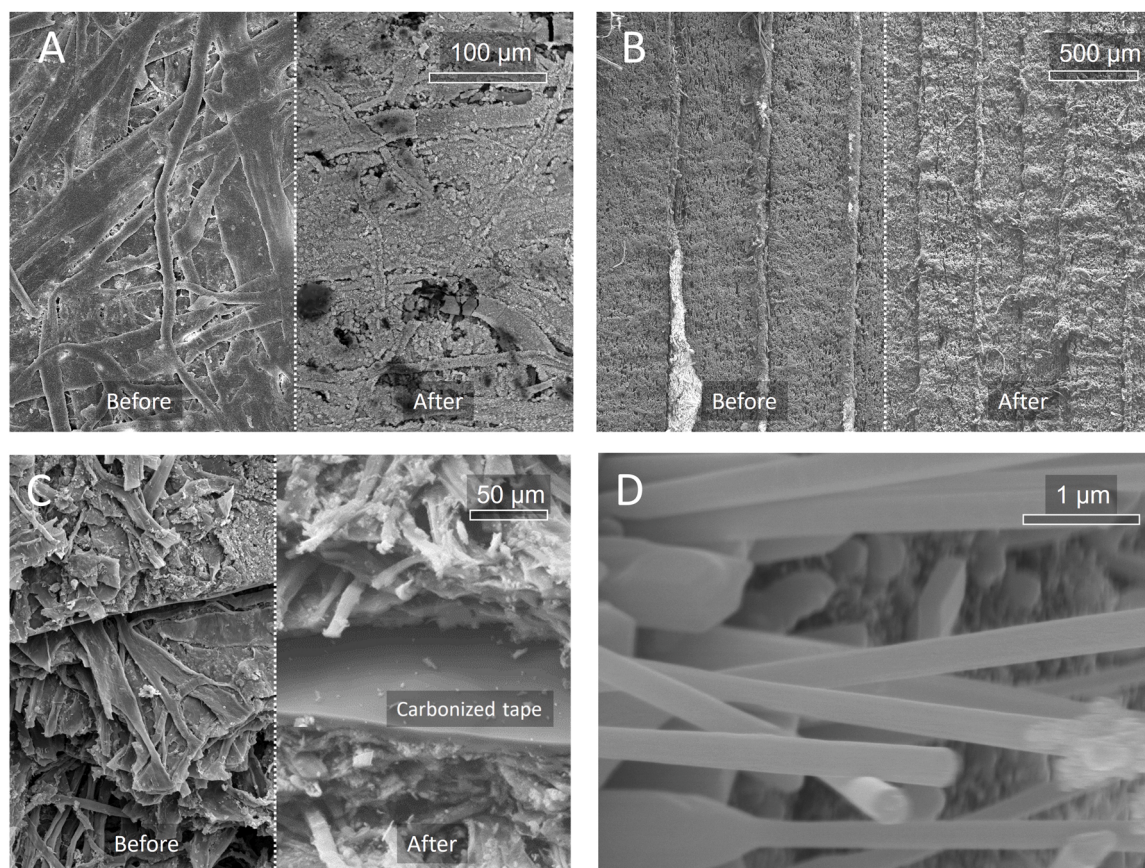


Fig. 3. (A) Top view (B) side view and (C) cross-sectional SEM images of the kraft paper and acrylic tape before and after carbonization. (D) Magnified view of carbonized nanocellulose fibrils.

curves at small strain was used to calculate the modulus, while the strength was estimated using the 0.2% offset method.

3. Results

For the present investigation, solid kraft paper cube, open cell square honeycombs (Square HC) and triangle honeycombs (Triangle HC), as well as closed cell Plate Simple Cubic (Plate SC), Plate Octet Truss (Plate OT) and Plate Simple Cubic – Octet Truss (Plate SC-OT) lattices were fabricated using ERASL and pyrolyzed at a maximum temperature of 1200 °C in the presence of Ar to produce Paper-Derived Architected Carbon Foams (PDACF) (Appendix A1). The lattice designs selected were of varying isotropy, to investigate its effect on the mechanical properties of the PDACFs.

Despite an overall volume shrinkage of $64.8 \pm 1.5\%$, the architected carbon foams maintained very good fidelity to the original CAD designs even after pyrolysis (Fig. 2; Appendix A2). Using helium gas pycnometry, the porosity of the carbonized kraft paper, which had an apparent density of $561.7 \pm 3.1 \text{ kg/m}^3$, was determined to be $\sim 74.5\% \pm 1.4\%$. Combined with macroscopic lattice porosities of 20–70% introduced to the structures via additive manufacturing, the PDACF achieved overall porosities of 79–92% (Appendix A3). An attempt to measure the surface area of the PDACF fibers was also made, but the nitrogen adsorption-desorption isotherms obtained did not follow a Type II profile and hence, no quantitative values were forthcoming based on the BET analysis (Appendix A4).

3.1. Microstructure

Microscopic examination of the kraft paper before and after carbonization showed that the kraft fibers shrunk and seemingly fused

together as it became harder to identify the outline of individual fibers (Fig. 3A). In addition, the shrinkage of the acrylic adhesive along the thickness dimension, from $\sim 100 \mu\text{m}$ to $\sim 15 \mu\text{m}$ (85%), was observed to be greater than that of the kraft paper, from $\sim 500 \mu\text{m}$ to $\sim 350 \mu\text{m}$ (30%) (Fig. 3B). This indicates that there was much less carbonizable content in the adhesive material, which is in line with previous thermogravimetric analysis (TGA) results for acrylic [42]. Nevertheless, the carbonized tape maintained its morphology as a thin continuous film and remained bonded with the kraft fibers, conferring structural integrity to the PDACF (Fig. 3C). It is also clear from the microscopy images that the kraft fibers were all randomly aligned in the plane of the paper sheet and there were virtually no fibers oriented in the z-axis (i.e. build direction), parallel to the sheet thickness. Furthermore, a closer inspection of the kraft fibers in certain regions reveal carbonized nanocellulose fibrils with $\sim 100 \text{ nm}$ diameter (Fig. 3D), indicating that the hierarchical structure of kraft fibers was intact even after carbonization, down to the nanoscale.

Although the macroscopic texture of the plain carbonized kraft paper and plain carbonized acrylic tape appear to be very different (Fig. 4A and B insets), their Raman spectra were remarkably similar, with I_D/I_G ratios of 2.2 and 3.2 respectively (Fig. 4A and B). The transformation of cellulose in the kraft paper and acrylic to graphite in the adhesive tape can be clearly observed in the X-ray diffraction (XRD) spectra (Fig. 4C). With the exception of additional peaks caused by calcium carbonate additives, which are often added to paper to improve their opacity, printability, brightness and fiber coverage [43], as well as alumina impurities from the sample holder in the furnace, the cellulose and acrylic spectra agree very well with previous reports [44,45]. After pyrolysis, the spectra of the carbonized paper and carbonized tape clearly exhibited the characteristic (002) peak and (10)-band peak commonly observed in graphite [46].

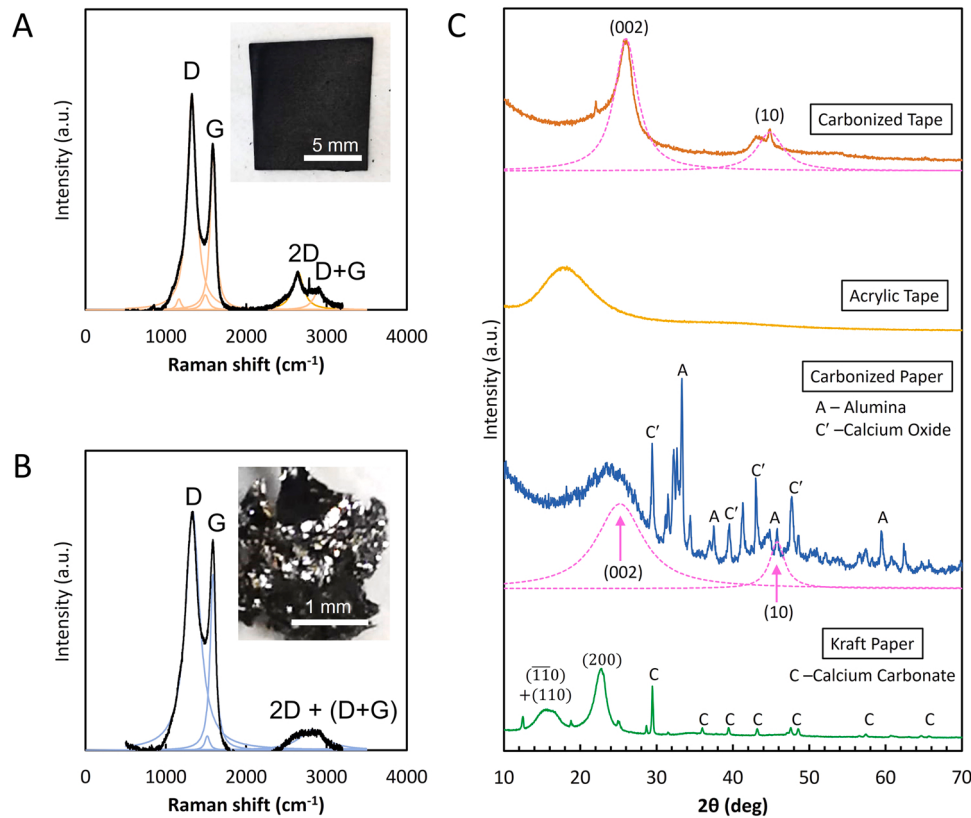


Fig. 4. Raman spectrum and deconvoluted peaks of (A) plain carbonized paper (B) plain carbonized acrylic tape. (C) XRD spectra and deconvoluted peaks of kraft paper, carbonized kraft paper, acrylic tape and carbonized acrylic tape.

Table 1

Calculated dimensions of nanographite crystallites.

	L_a (nm)	L_c (nm)	c (nm)
Carbonized kraft paper	17.2	1.00	0.353
Carbonized acrylic tape	11.6	2.17	0.343

The size, L_a , thickness, L_c , and interlayer spacing, c , of the nanographite crystals in the carbonized paper and tape can be determined (Table 1) by applying the general Tuinstra-Koenig's law [47] to the Raman spectra,

$$L_a(\text{nm}) = (2.4 \times 10^{-10}) \lambda_i^4 \left(\frac{I_G}{I_D} \right) \quad (1)$$

where λ_i refers to the excitation laser wavelength in nm, and the Scherrer equation [44] to the XRD spectrum of the carbonized materials,

$$L_c(\text{nm}) = \frac{K \lambda_X}{\beta \cos \theta} \quad (2)$$

where $K = 0.9$, λ_X refers to the X-ray excitation wavelength in nm and β refers to the width (in radians) at half height of the (002) peak. θ refers to the Bragg angle, which can be used to determine the distance between the graphite layers, c , through the following relationship,

$$c = \frac{\lambda_X}{2 \sin \theta} \quad (3)$$

While the presence of graphite nanocrystals, together with a skeletal density of 2.2 g/cm^3 obtained from gas pycnometry, appear to imply that the carbonized kraft paper was purely graphitic, detailed HRTEM studies have shown that carbonized cellulose is composed of small regions of graphite/ graphene nanocrystals, fullerenes, disordered carbon

and turbostratic carbon formed by pentagonal and heptagonal bonding of sp^2 carbon [48,49]. Therefore, the skeletal density, which is in line with results for carbonized cellulosic plant matter [50], is most likely a composite figure from these different carbon allotropes, much like glassy carbon (i.e. vitreous carbon), which is known to exhibit Raman spectra very similar to those in Fig. 4A and B [51,52]. While details of carbonized acrylic are scarce in the literature, the similarity of its Raman and XRD spectra to those of carbonized cellulose suggests that its atomic structure is likely a complex mix of carbon allotropes as well. Because the full identification of the various forms of carbon present in the pyrolyzed kraft paper can be challenging and not as crucial to the present investigation, it would be best addressed in a separate study.

3.2. Electrochemical storage property

The results from Li-ion battery tests conducted on the carbonized paper and carbonized paper and tape composite appear to support this premise as the specific capacity of the carbonized kraft paper, $\sim 140 \text{ mAh/g}$ when cycled at a specific current of 10 mA/g (Fig. 5 A and B), falls short of the $350\text{--}370 \text{ mAh/g}$ that graphite electrodes typically exhibit, but is very much in line with those of pyrolyzed polymer foams, that had graphitic clusters embedded within a matrix of disordered carbon [12]. The addition of the carbonized tape worsened this capacity to $\sim 80 \text{ mAh/g}$ ($\sim 65 \text{ mAh/g}$ after 300 cycles), likely because the continuous sheet of tape decreased the surface area to volume ratio of the sample and Li ions could only access and react with the surface of the carbonized tape. Nevertheless, the cycling of the carbonized materials has shown to be stable, with 100% Coulombic efficiency, up to 300 cycles indicating that they are suitable for sustained usage. This stability can be attributed to the lack of observable degradation in the carbonized fibers, despite the many cycles of lithiation and delithiation (SEM images in Fig. 5B).

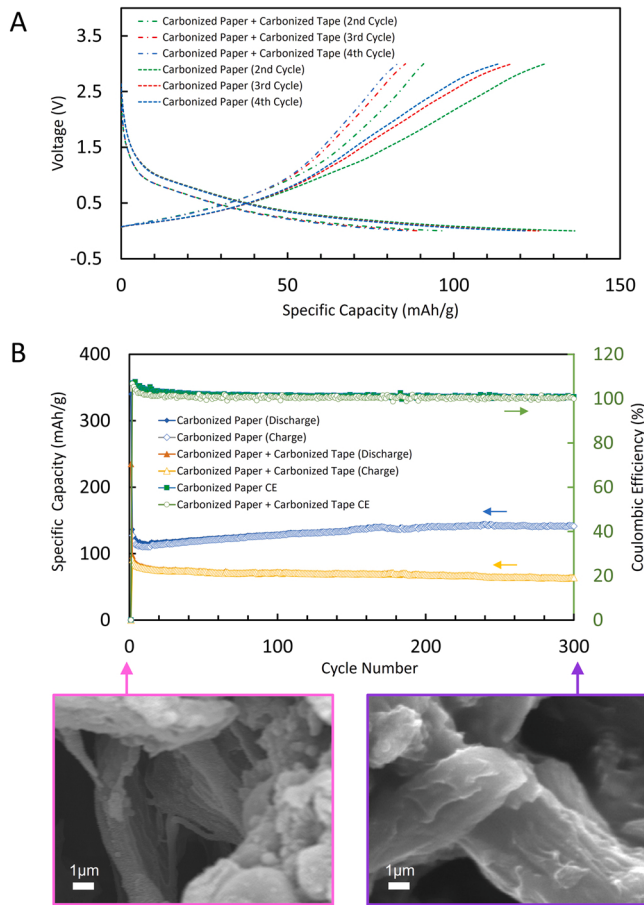


Fig. 5. (A) Galvanostatic charge – discharge voltage profiles of 3 early cycles for a single layer of carbonized kraft paper (solid lines) and carbonized kraft paper with acrylic tape (dashed lines) (B) Specific capacity and coulombic efficiency of the carbonized materials as a function of cycle number. SEM images of the carbonized fibers before (0th cycle) and after battery cycling tests (300th cycle) are also shown.

3.3. Compressive stress - strain response

Because the samples were constructed with layers of paper and adhesive using ERASL, the properties of the architected carbonized foams were expected to be anisotropic. This anisotropy was further enhanced as the carbonized fibers only lie in the plane of the paper sheet and not out-of-plane. Unlike structures with cubic or higher orders of symmetry, the elastic modulus of such anisotropic structures in different directions cannot be easily computed analytically [53]. Therefore, compressive tests were experimentally conducted in 2 major axes - one that was perpendicular to the paper layers *i.e.* Reuss/ isostress orientation (Fig. 6A) and the other, parallel to the layers *i.e.* Voigt/ isostrain orientation (Fig. 6B). Interestingly, in each orientation, several similarities can be drawn across all the structures.

For the *Perpendicular* orientation (Fig. 6A), the stress in the lattices was observed to rise gently to a maximum value up to a strain of $\sim 30\text{--}40\%$, before dipping and plateauing. It then increased again as the densification phase began at $\sim 50\text{--}70\%$ strain. The stress in these PDACFs did not reach 0 MPa at any point during the compression process, indicating that the lattices and cubes maintained some level of structural integrity throughout.

In contrast to this ductile-like failure, stress for the PDACFs in the *Parallel* orientation was observed to rise rapidly within a small strain ($\leq 5\%$) before gently decreasing, in most cases, to 0 MPa by $30\text{--}40\%$ strain (Fig. 6B). The lattices, with the exception of Plate SC-OT, exhibited no load-bearing capacity from 40% strain onwards (*i.e.* stress remained at

0 MPa), until densification began at $> 70\%$ strain. Such a failure progression resembles the brittle failure typically observed in ceramics [54]. Regardless of the apparent ductile or brittle failure modes exhibited at the macroscopic level, SEM examination of the failed PDACF surfaces revealed sharp faceted edges, a clear indication that the carbonized fibers failed through brittle fracture (Fig. 6C).

To better understand the macroscopic orientation-dependent failure mode of the PDACFs, the von Mises stress distributions of the cube structure were first examined. For the *Perpendicular* case, the layers were stacked along the *y*-axis and thus, the stress distributions in the *x*-*y* and *y*-*z* planes were the same, with the greatest intensity found in the center spot of each plane (Fig. 6D). Experimentally, the failure of the cube PDACF was found to be associated with the expulsion of fine black dust (black arrows in Fig. 6A), indicating that a large multitude of microscopic fractures had taken place within the structure, pulverizing the carbonized kraft fibers and tape into fine bits. As the compressive strain increased, larger chunks of materials were violently expelled as well. This energetic ejection of material suggests that substantial elastic energy was stored within the structure before being released during the failure of the structure, which may not be surprising given that the linear elastic regime of the *Perpendicular* PDACF cube reached $\sim 30\%$ strain.

In the *Parallel* orientation, the layers were stacked in the *z*-axis, which led to a difference in the stress distributions in the *x*-*y* and *y*-*z* faces (Fig. 6E). In the *x*-*y* face, which was 2D isotropic, the stresses were mainly concentrated along the diagonal shear bands. In the *y*-*z* face, however, the stresses were concentrated along the top and bottom edges (red arrow in Fig. 6E). This result arises directly from imposing a fixed *x* and *z* position on the top and bottom faces of the PDACF cube to simulate the compressive testing process. To maintain $\Delta x = 0$ and $\Delta z = 0$, the platen had to exert a shear stress in τ_x in the *x*-axis and τ_z in the *z*-axis. Because G_{xy} was higher than G_{yz} due to the stacking of the layers in the *z*-axis, τ_x had to be greater than τ_z to maintain the fixed horizontal position of the top and bottom surfaces, leading to the high stress levels found at the top and bottom edges of the *y*-*z* faces. This, in turn, caused the layers to begin delaminating from the top/ bottom edge, which was the main cause of failure in the *Parallel* PDACF cube (Fig. 6B). As the cube was further compressed, it split into individual layers incapable of bearing load. If delamination propagated through an entire layer, it could be expelled as well (black arrows in Fig. 6B).

Unlike the *Perpendicular* cube, compression in the *Perpendicular* orientation of the triangle honeycombs led to stress concentrations only in the inner walls of the structure (red arrow in Fig. 7A). Consistent with this simulated stress distribution, there was no experimental observations of material expulsion at the point of failure. Instead, it appeared that failure was precipitated by the buckling of the honeycomb cells and associated fractures at high strains.

The square honeycombs, on the other hand, when compressed in the *Parallel* orientation, exhibited the same stress distribution as *Parallel* cube *i.e.* intense stresses at the top and bottom edges of the *y*-*z* faces (red arrow in Fig. 7B). Consequently, the failure process for square honeycombs was similar to that of the cube – initiation of layer delamination from the bottom edge at a small strain and propagation through the layers (yellow arrows in Fig. 7B), leading to the splitting of the structure into individual layers incapable of bearing load due to a lack of structural integrity.

For the *Perpendicular* Plate Simple Cubic structures, the simulated stress distribution indicates that the maximum stresses were sustained on the side faces of the closed cells (black arrow in Fig. 8A). This was verified experimentally, as the walls of two closed cell were observed to rupture at a strain of 47% and 57% respectively, exposing the inner chambers (yellow arrows in Fig. 8A).

In the *Parallel* orientation, the maximum stresses were once again observed to be along the top and bottom edges of the *y*-*z* faces. As a result, delamination of the layers in the *y*-*z* planes was observed, as with the other structures. The difference for Plate Simple Cubic, however, was that the structure did not dissociate into individual layers, as the

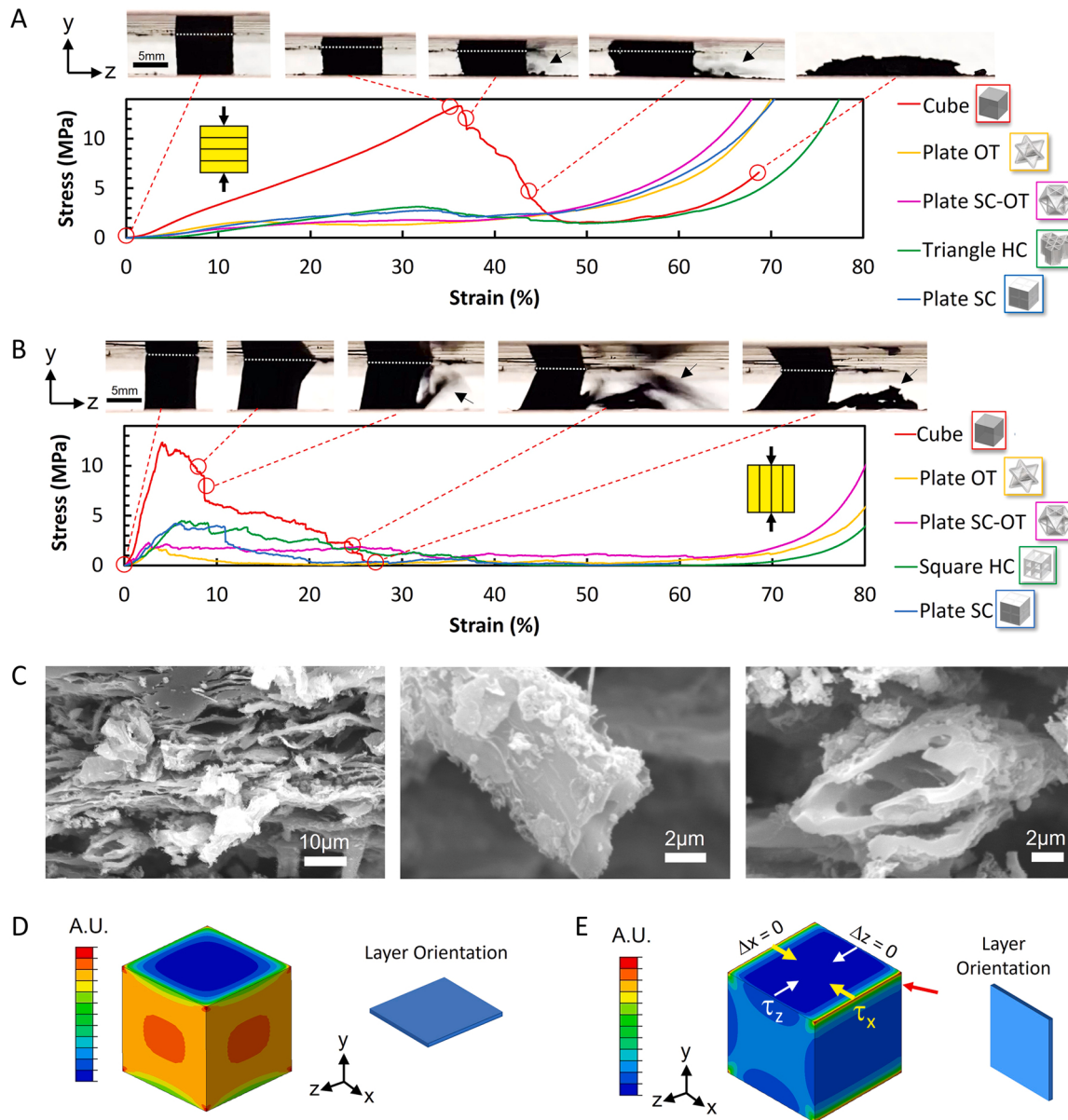


Fig. 6. Engineering stress – strain response of compression tests on PDACF in the orientations where the layers are (A) perpendicular and (B) parallel to the load direction (*i.e.* y -axis), as illustrated schematically in the insets. The data depicted here pertain to structures with lattice relative densities of 0.5–0.7. The lattice relative density of the cubes is 1. The photographic images show the failure process of the cubes at various strain levels. The white dotted lines indicate the top boundary of the lattice, above which is simply a reflection of the lattice on the compression platen. (C) SEM images of failed PDACFs at different magnifications. Clean, faceted edges can be observed for individual fibers, indicating that they had failed through brittle fracture. Simulated von Mises stress distribution in the cube structure for the (D) perpendicular and (E) parallel orientations.

empty spaces within the geometry prevented the delamination cracks from propagating straight through the structure. Instead, the delaminated layers were observed to buckle partially as the compression proceeded further (yellow arrows in Fig. 8B).

With the *Perpendicular* Plate Octet Truss, maximum stress was observed in 2 distinct locations, at the top/ bottom edges and middle edges, which were labeled as ‘a’ and ‘b’ in Fig. 9A for easy reference. Experimentally, fractures were clearly observed to initiate and propagate from the 4 locations of ‘a’ (2 top and 2 bottom) visible within one y - z face (yellow arrows in Fig. 9A). Any fracture emanating from location ‘b’ could not be observed or ascertained in the y - z plane.

Interestingly, the locations of highest stresses in the *Parallel* orientation were the same as those in the *Perpendicular* orientation for Plate Octet Truss. Unlike the *Perpendicular* orientation, however, delamination of the layers due to fracture initiation and propagation from

location A, as well as that from location B, could be clearly observed in the *Parallel* orientation (yellow arrows in Fig. 9B).

Similar to Plate Octet Truss, the maximum stress for *Perpendicular* Plate Simple Cubic – Octet Truss was present in 2 features of the geometry, (a) the triangular face and (b) the vertical plate (Fig. 10A). However, lattice failure was observed to be precipitated primarily by a fracture through the triangular face at 29% strain, while failure of the vertical plate, in the y - z plane at least, was not present.

For the *Parallel* orientation, the maximum stresses for Plate Simple Cubic – Octet Truss were located at (a) top/ bottom edge of the vertical plate in the y - z face and (b) middle of the vertical plate in the x - y face (Fig. 10B). At the point of lattice failure, the structure was observed to fracture at location ‘a’ while buckling occurred at the side, in the x - y face, possibly indicating a failure at location ‘b’. At higher compressive strains, some layers were completely delaminated (green arrows in

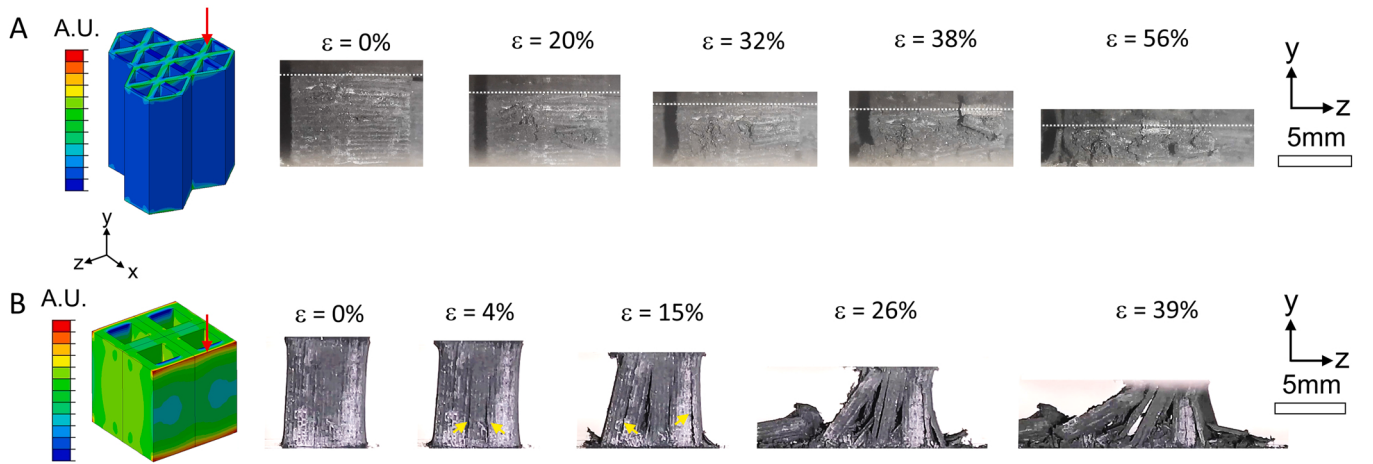


Fig. 7. Simulated von Mises stress distribution and experimental images depicting the deformation of the (A) Triangle Honeycombs (stacking direction: y-axis) and (B) Square Honeycombs (stacking direction: z-axis) at different strains. Compression testing was conducted along the y-axis. The white dotted lines indicate the top boundary of the lattice, above which is simply a reflection of the lattice on the compression platen.

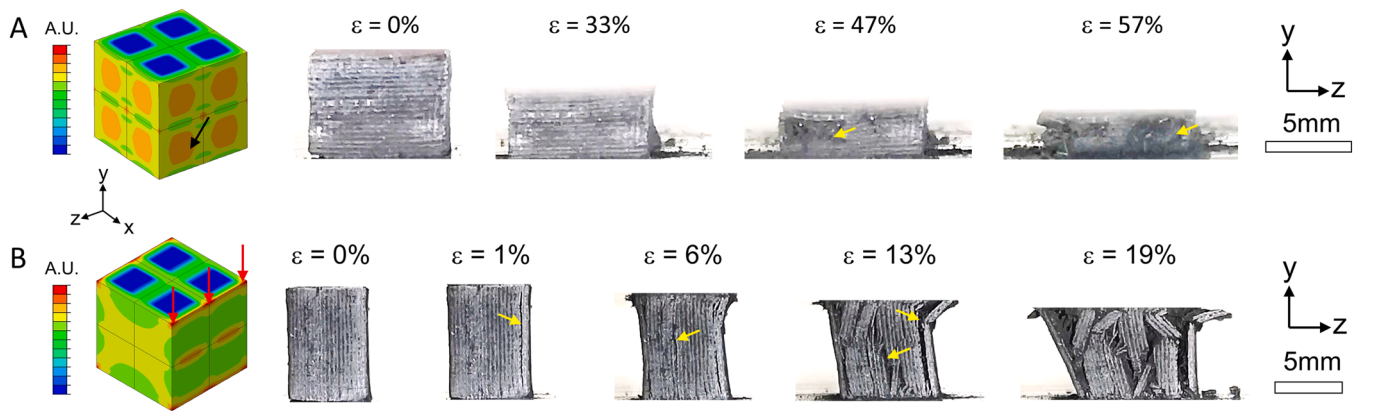


Fig. 8. Simulated von Mises stress distribution and experimental images depicting the deformation of the Plate Simple Cubic lattice at different strains in the (A) Perpendicular (stacking direction: y-axis) and (B) Parallel (stacking direction: z-axis) orientations. Compression testing was conducted along the y-axis.

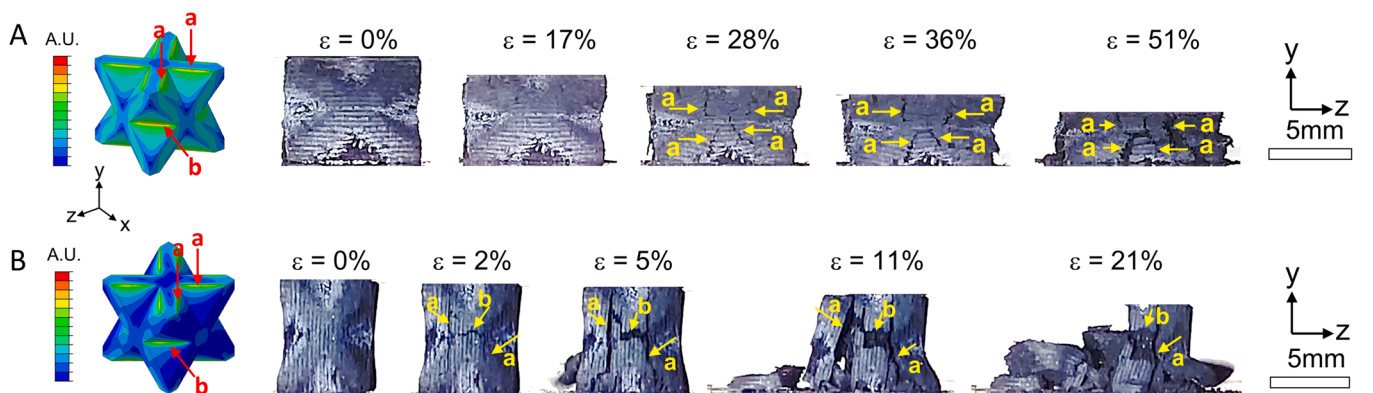


Fig. 9. Simulated von Mises stress distribution and experimental images depicting the deformation of the Plate Octet Truss lattice at different strains in the (A) Perpendicular (stacking direction: y-axis) and (B) Parallel (stacking direction: z-axis) orientations. Compression testing was conducted along the y-axis.

Fig. 10B), but otherwise, the Plate Simple Cubic – Octet Truss geometry remained mostly intact and continued to carry load, unlike the case with other Parallel structures.

3.4. Compressive resilience during cyclic loading

One notable result from the compressive stress-strain response of the

PDACFs is that the peak stresses for the *Perpendicular* orientation occurred at $\sim 30\%$ strain or above, which is a remarkable display of compressive resilience for the inherently brittle carbonized fibers. To further investigate this property, cyclic loading to sequentially higher strains (e.g. $0\% \rightarrow 10\% \rightarrow 0\% \rightarrow 20\%$ etc.) was performed (Fig. 11).

Consistent with the behavior of graphene aerogels [19,20], the loading curve of each cycle was able to re-trace the unloading curve of

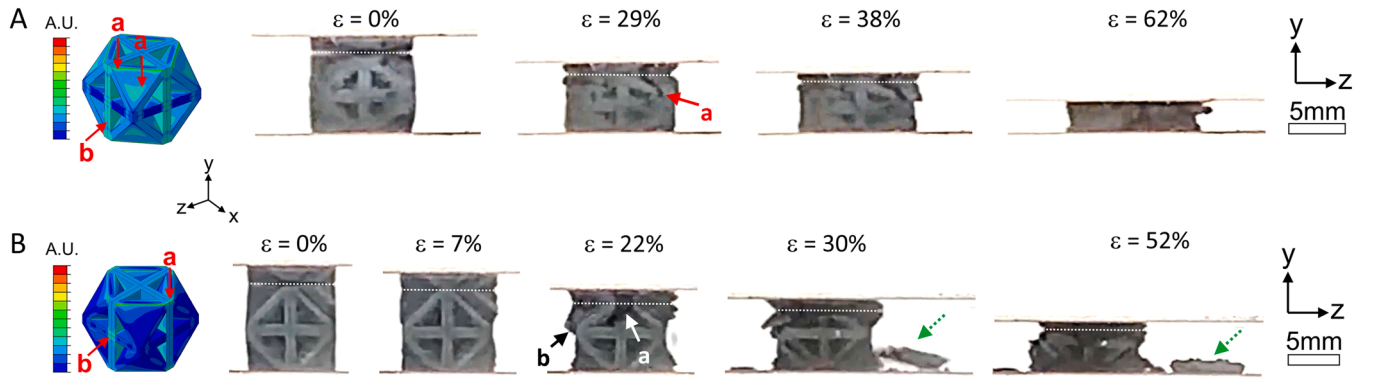


Fig. 10. Simulated von Mises stress distribution and experimental images depicting the deformation of the Plate Simple Cubic - Octet Truss lattice at different strains in the (A) Perpendicular (stacking direction: y-axis) and (B) Parallel (stacking direction: z-axis) orientations. Compression testing was conducted along the y-axis. The white dotted lines indicate the top boundary of the lattice, above which is simply a reflection of the lattice on the compression platen.

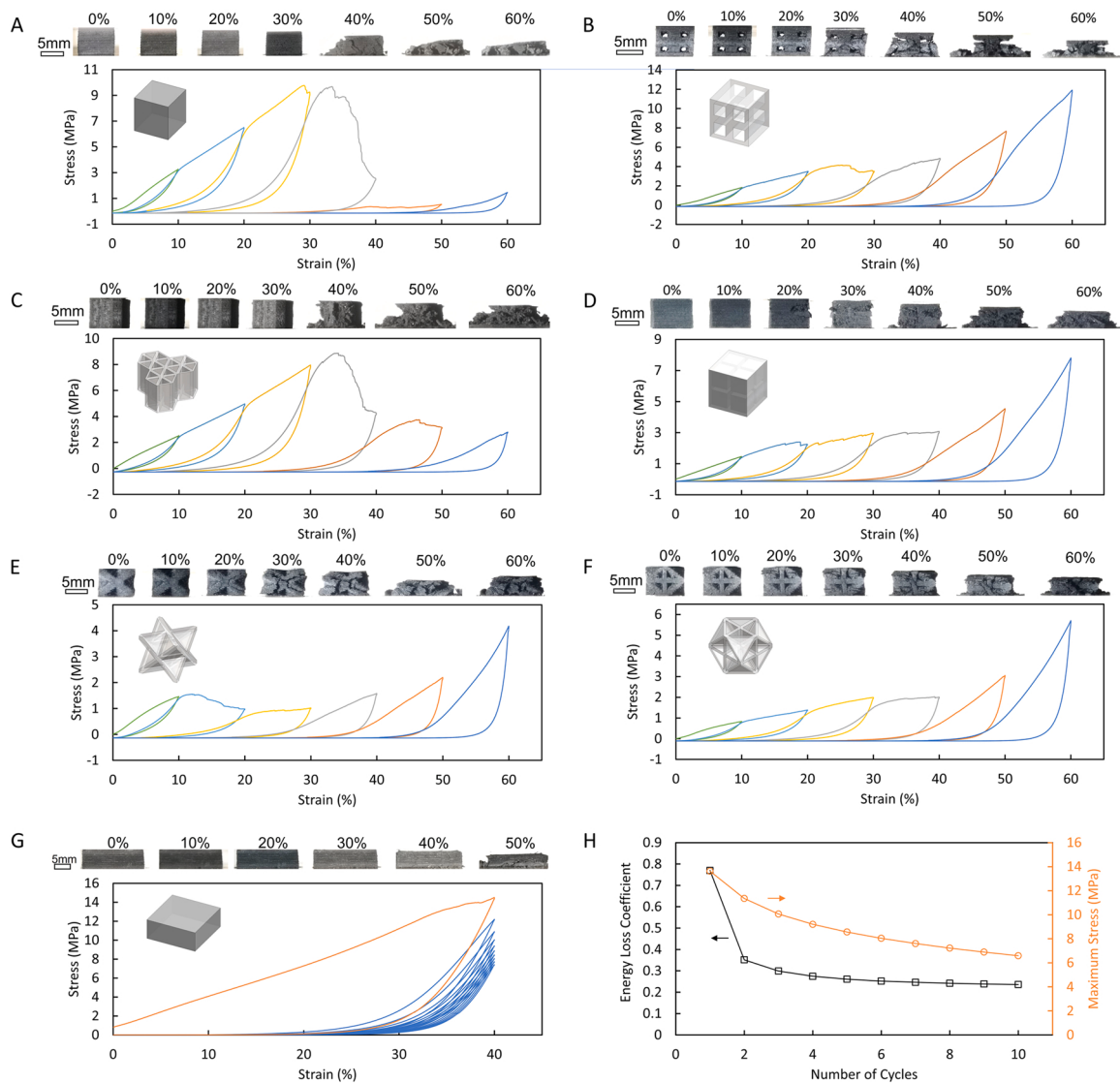


Fig. 11. Cyclic loading stress-strain response of PDACF (A) Cube (B) Square Honeycombs (relative density = 0.84) (C) Triangle Honeycombs (relative density = 0.82) (D) Plate Simple Cubic (relative density = 0.66) (E) Plate Octet Truss (relative density = 0.69) (F) Plate Simple Cubic-Octet Truss (relative density = 0.62). Photographs above each plot depict the unloaded PDACF structures after they have been compressed to the strain indicated above each image. (inset) Schematic illustration of each geometry. (G) Cyclic loading of cuboid for 10 cycles. The cuboid has a height to width ratio of 0.3. (H) Energy loss coefficient and the maximum stress sustained by the cuboid as a function of cycle number. The PDACF layers were horizontal while the load axis was vertical for all geometries.

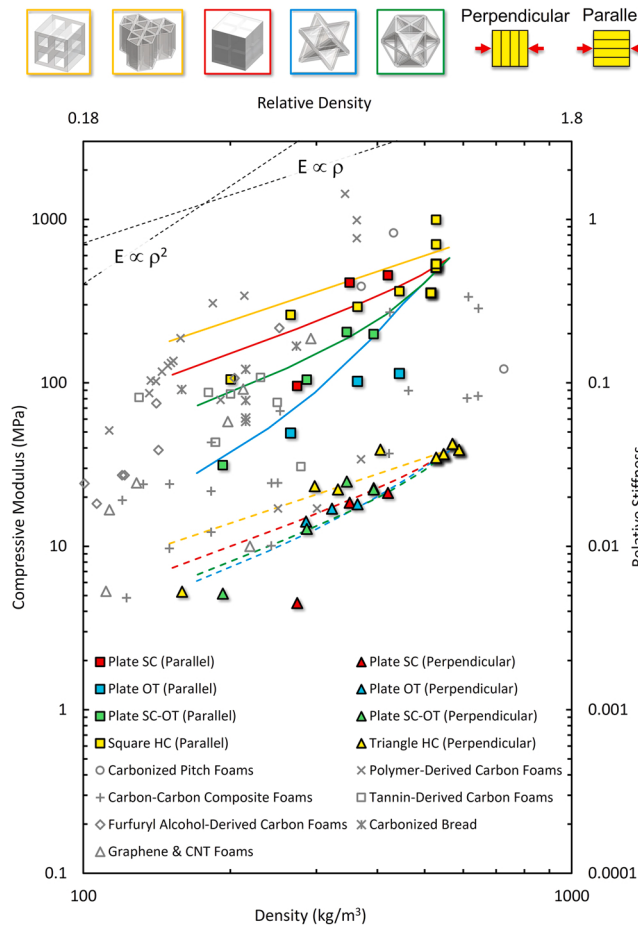


Fig. 12. Plot of compressive modulus vs density, comparing PDACFs with conventional carbon pitch foams [32,33,55–57], polymer-derived carbon foams [17,30,58–60], carbon-carbon composite foams [61,62], tannin - derived carbon foams [63,64], furfuryl alcohol - derived carbon foams [31], carbonized bread foam [13] and graphene/ carbon nanotube (CNT) foams/ aerogels [15, 20,65]. Tannin, furfuryl alcohol and bread are plant derivatives and can be considered as renewable bioresources. Simulation data are represented by the solid (*Parallel*) and dashed (*Perpendicular*) lines.

the previous cycle before extending to a higher strain for all PDACF geometries. Moreover, the structures were observed to exhibit significant elastic recovery even at fairly high strain. For instance, the PDACF cube recovered $\sim 15\%$ strain after being compressed to 30% (Fig. 11A). Photographic evidence shows that most of the lattices do not look very different from their original state until they have been compressed to $\sim 30\text{--}40\%$, at which point significant fractures set in and irreversibly altered the lattice geometries (Fig. 11A - F).

Furthermore, when a flat PDACF cuboid was subjected to cyclic compression up to 40% strain (Fig. 11G; Appendix A5), its energy loss coefficients were observed to follow very closely to those of graphene aerogels [20], beginning with a value of $\sim 80\%$ for the first cycle, falling to $\sim 30\%$ by the third cycle and settling at $\sim 25\%$ for the rest of the cycles (Fig. 11H). The energy loss coefficient is given by

$$\text{Energy loss coefficient} = \frac{\text{area under loading curve} - \text{area under unloading curve}}{\text{area under loading curve}} \quad (4)$$

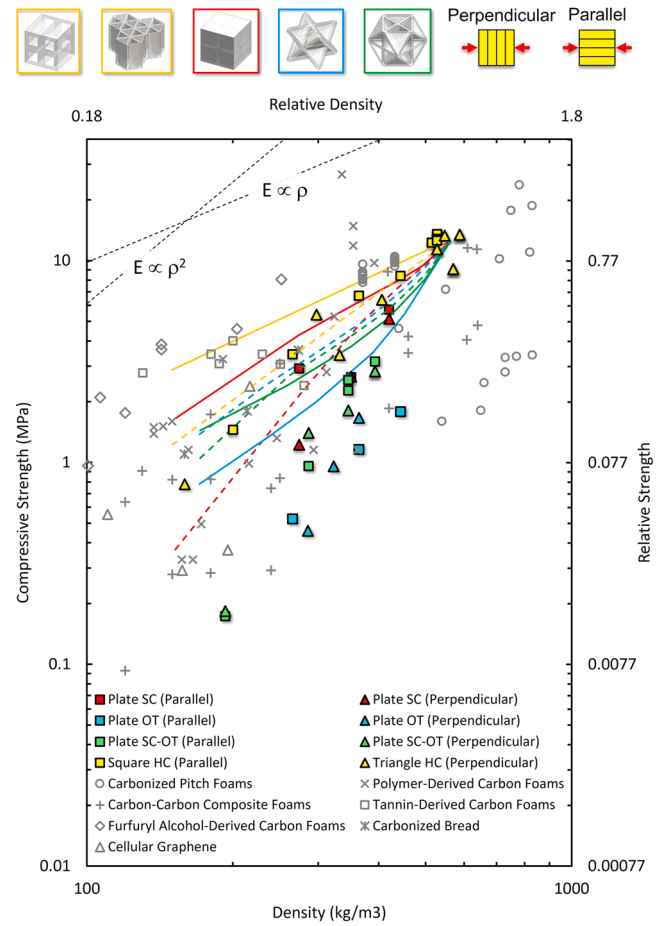


Fig. 13. Plot of compressive strength vs density, comparing PDACFs with conventional carbon pitch foams [32,33,55–57], polymer-derived carbon foams [17,30,58–60], carbon-carbon composite foams [61,62], tannin - derived carbon foams [63,64], furfuryl alcohol - derived carbon foams [31], carbonized bread foam [13] and cellular grapheme [15]. Simulation data are represented by the solid (*Parallel*) and dashed (*Perpendicular*) lines.

The elastic strain limits of 30–40% found here is consistent with that observed for the non-cyclic tests on PDACFs (Fig. 6). Although these limits may seem small compared to superelastic strains of 50% [20] to 90% [18,21] exhibited by graphene aerogels, the compressive resilience of PDACFs remains notable because they were obtained at stresses up to ~ 3 orders of magnitude higher. To the best of our knowledge, such recovery levels have yet to be reported for conventional carbon foams with comparable modulus and strength.

3.5. Mechanical properties

The modulus, strength and energy absorption properties of the PDACFs are compared to porous carbon materials obtained from conventional top-down and bottom-up approaches in Fig. 12–15.

3.5.1. Modulus

From Fig. 12, it can be observed that PDACFs were stiffer in the *Parallel* orientation (square data points) than the *Perpendicular*

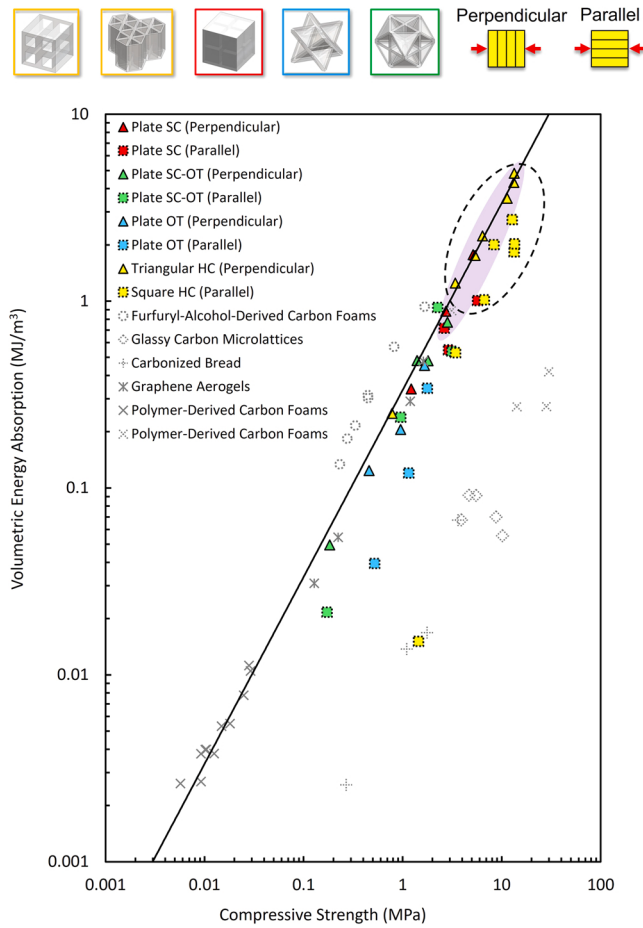


Fig. 14. Plot of volumetric energy absorption vs compressive strength, comparing PDACFs with conventional polymer-derived carbon foams (broken borders) [17,30,58], polymer-derived carbon foams (solid borders) [59,60], furfuryl alcohol - derived carbon foams [31], carbonized bread foam [13], glassy carbon microlattices [67] and graphene aerogel [20]. Tannin, furfuryl alcohol and bread are plant derivatives and can be considered as renewable bioresources. Broken borders for data points indicate brittle fracture before 15% strain.

orientation (triangle data points). This is in line with the results from simulations, which expected a clear segregation between the moduli of the *Parallel* orientation (solid lines) and the *Perpendicular* orientation (dashed lines). The simulations also predict that the modulus would decrease in the following order: Honeycombs, Plate Simple Cubic, Plate Simple Cubic – Octet Truss and Plate Octet Truss. Practically, however, the uncertainty in the experimental results obscured any differences between the *Perpendicular* geometries, although the sequence was broadly observable for the *Parallel* geometries, with Plate Octet Truss (blue squares) exhibiting the lowest moduli, followed by Plate Simple Cubic – Octet Truss (green squares).

Importantly, Fig. 12 clearly shows that the modulus of carbon aerogels (grey triangles) fall short of the levels achievable by the PDACF in the present study. In fact, there were relatively few data points that even had modulus and strength in the MPa range for comparisons to be made, despite the abundance of literature on carbon aerogels. This clearly

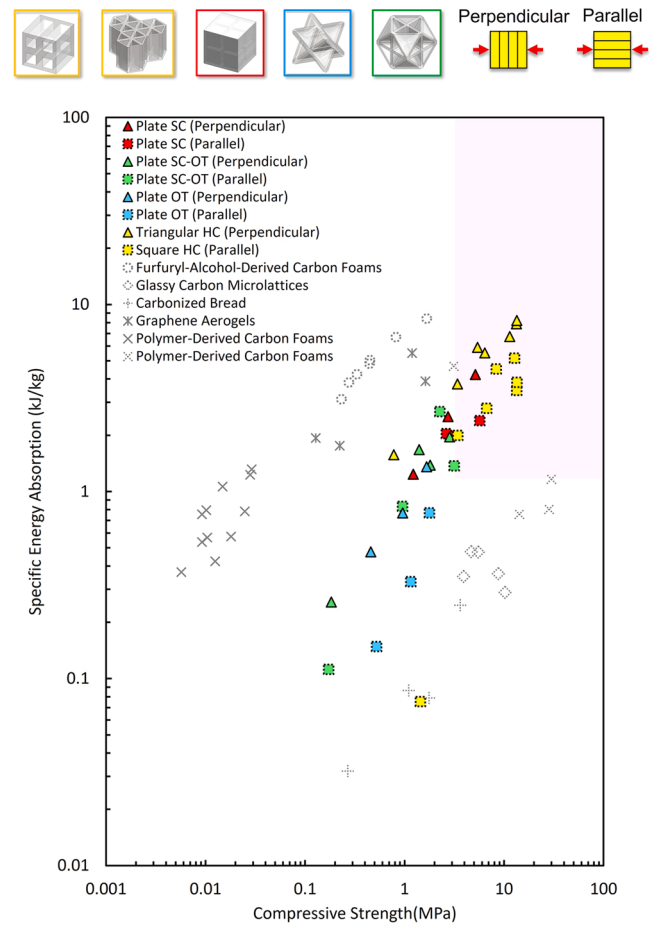


Fig. 15. Plot of specific energy absorption vs compressive strength. PDACFs are compared to conventional polymer-derived carbon foams (broken borders) [17, 30,58], polymer-derived carbon foams (solid borders) [59,60], furfuryl alcohol - derived carbon foams [31], carbonized bread foam [13], glassy carbon microlattices [67] and graphene aerogel [20]. Tannin, furfuryl alcohol and bread are plant derivatives and can be considered as renewable bioresources. Broken borders for data points indicate brittle fracture before 15% strain.

demonstrates the limitations of using bottom-up techniques to produce structural carbon materials.

Compared to carbon foams fabricated using top-down methods, the moduli of the PDACF also hold up well. Outside of a few phenolic- and melamine- derived carbon foam samples, the best of the PDACFs, namely *Parallel* Square Honeycombs (yellow square data points and yellow solid line) and *Parallel* Plate Simple Cubic (red square data points and red solid line) architectures exhibited some of the stiffest values reported for carbon foams in the density range of 100 – 800 kg/m³.

3.5.2. Strength

Unlike the case with modulus, there was no significant difference between the strengths in the *Parallel* and *Perpendicular* orientations for a given PDACF lattice geometry (colored datapoints in Fig. 13). This is expected since the PDACF cubes exhibited similar failure stresses in different orientations (see Fig. 6 for example). In other words, the PDACF structures displayed anisotropic stiffness and isotropic strength.

Experimentally, Honeycombs (yellow data points) exhibited the highest strength, which were amongst the best in the literature for porous carbon materials. This was followed by Plate Simple Cubic (red data points), Plate Simple Cubic – Octet Truss (green data points) and Plate Octet Truss (blue data points). The actual strength of high-density Honeycombs and Plate Simple Cubic structures were reasonably close to the simulated data (yellow and red trendlines). However, experimental values low-density lattices, as well as Plate Simple Cubic – Octet Truss and Plate Octet Truss, generally fell short. This could be due the introduction of defects during the fabrication process, which the complex geometries of Plate Simple Cubic – Octet Truss and Plate Octet Truss may be more sensitive to. There was also a higher chance of defect generation when the laser was cutting out the thin walls in low-density lattices during the ERASL additive manufacturing process. These defects then became nucleation points for fracture initiation, which led to lattice failure.

3.5.3. Energy absorption

While the PDACFs exhibited good moduli and strengths, energy absorption is where they really excel compared to current porous carbon materials. Because energy absorption is a function of strain and different materials have an optimal stress for dissipating energy [66], in the interest of fairness, we have chosen to compare the energy absorption at the point of highest maximum energy efficiency for each material. The energy absorption per unit of apparent volume, Q_v , is then given by

$$Q_v = \int_0^{\varepsilon_0} \sigma d\varepsilon \quad (5)$$

where σ refers to stress and ε_0 refers to the strain that corresponds to the point of highest energy absorption efficiency of the material, which usually happens to be the densification strain. The energy absorption efficiency, η , is the inverse of cushion factor, C , and can be expressed as [22,66].

$$\eta_v = \frac{1}{C} = \frac{Q_v}{\sigma_{max}} \quad (6)$$

where σ_{max} refers to the maximum stress sustained by the material up to the strain of ε_0 . σ_{max} is typically equivalent to the compressive strength of the material.

Based on the literature, it is well-known that graphene aerogels and lightweight carbon foams possess excellent elastic recovery for repeated usage in energy dissipation applications, but they exhibit low compressive strengths, which also limit their energy absorption levels (grey data points with solid borders in Fig. 14). On the other hand, high density carbon foams produced through various top-down techniques typically exhibit brittle failure beyond $\sim 10\%$ strain, limiting their energy dissipation properties to single-use, even though their volumetric energy absorption and compressive strength can be 1–2 orders of magnitude higher (grey data points with broken borders in Fig. 14).

In contrast, PDACFs can achieve both the compressive resilience of aerogels and the large compressive strength and volumetric energy absorption of high-density carbon foams. In particular, the samples highlighted in purple in Fig. 14 displayed a combination of elastic recovery, volumetric energy absorption and strength that has not been achieved before. Even if the property of compressive resilience is neglected, a number of PDACF geometries (encircled by the dashed line) have also displayed unprecedented volumetric energy absorption levels for compressive strength ranging from $\sim 3 - 13$ MPa. The average energy

absorption efficiency of PDACFs can be estimated from the best fit trendline (black), which exhibits a slope of 0.334. According to Eq. (6), the energy absorption efficiency of PDACFs is then 33.4% (cushion factor is 3), which is much higher than that of conventional carbon foams and closer to ductile and elastomeric polymer lattices [22,24].

Going further, the volumetric energy absorption was normalized by the mass density of the porous carbon materials to give the specific energy absorption,

$$Q_m = \frac{Q_v}{\rho} \quad (7)$$

where ρ represents the mass density of the porous material. The specific energy absorption is essentially the energy absorption per unit mass, which allows us to compare the energy absorption with respect to the actual volume of carbon material in a structure, rather than the apparent volume, as was the case with the volumetric energy absorption.

From Fig. 15, it is clear that current porous carbon materials generally fall in 2 distinct groups. The first group, composed exclusively of brittle carbon foams fabricated with the top-down approach, exhibits high compressive strength (> 3 MPa) and relatively low specific energy absorption (< 1 kJ/kg). The second group, which includes graphene aerogels, exhibits high specific energy absorption but low compressive strength. PDACFs were generally found to occupy the property space between these 2 groups, offering better specific energy absorption than brittle carbon foams and better strength than the resilient aerogels. A group of high-density Honeycombs, Plate Simple Cubic and Plate Simple Cubic - Octet Truss structures, in particular, exhibited both high strength and large specific energy absorption values that are not available with current porous carbon materials (highlighted in pink), demonstrating again, the value of PDACFs in extending the property space of porous carbon materials. Considering that these mechanical properties have yet to be optimized with respect to material parameters such as the thickness of kraft paper, there may be room for further improvement.

4. Discussion

Cellulose is a renewable, non-food-based resource and a natural carbon sink for trapping atmospheric carbon on land. The stored carbon, however, can be released back to the atmosphere if it is left to decay naturally. By pyrolyzing cellulose into a multi-functional structural material, its carbon can be stored permanently as a useful solid. In our current carbonization process, the mass shrinkage of cellulose was $77.1 \pm 1.6\%$, which meant that 23% of the cellulose was left as carbon in the PDACFs. Since the mass fraction of carbon in cellulose ($C_6H_{10}O_5$) is 44.4%, this implies that slightly more than half ($\sim 52\%$) of the carbon stored in the cellulose was permanently locked as PDACFs while the rest were lost as volatile oils and gases [38]. While it is regrettable that pyrolysis re-releases some of the carbon in cellulose into the atmosphere, from a material standpoint, the process remains carbon negative, as half of the atmospheric carbon captured by the plants in cellulose is retained on land. In contrast, the current use of fossil fuels and synthetic polymers as precursors for carbon foams is carbon positive, as it involves releasing carbon that is not captured from the atmosphere.

Cellulose fibers, when assembled into a paper form, is particularly suited to be a precursor for carbon foams due to the naturally occurring spaces between the loosely packed fibers. To architect the 3D paper-based cellulose structures for the production of carbon foams, ERASL, a sheet lamination additive manufacturing technique, was introduced.

Compared to traditional sheet lamination techniques such as LOM, ERASL presents several advantages.

Firstly, ERASL eliminates the need for post-print removal of excess material in the build. Secondly, the area removal approach improves the 3D printing resolution as it is easier to burn off small cavities than to cut and remove them from the build. Most importantly, ERASL also allows closed cell structures to be easily manufactured (Fig. 1A & C).

Closed cell geometries (e.g. plate lattices) are appealing for lightweighting purposes as recent studies have shown that they can offer better modulus and strength for the same material volume than truss lattices [26,68,69]. However, these structures are incompatible with nearly all conventional additive manufacturing techniques and any attempt to fabricate them would result in the trapping of precursor materials (e.g. unsintered powder, unpolymerized resins etc.) within the isolated air spaces. In LOM, for instance, it would not be possible to remove the excess material in the regions designated as voids as these cell cavities would be completely sealed. To circumvent this issue, researchers have been introducing holes to closed cell structures to release the trapped materials, turning the geometries into open cell designs and compromising their mechanical properties [26,68,70]. While recent studies have shown that material extrusion can be successfully employed to 3D print closed cell lattices without release holes [71,72], the technique is incompatible with paper sheets. Therefore, to date, ERASL remains the only technique that is able to realize true closed cell designs from paper sheets (Fig. 1 and Fig. 2).

Despite its multiple advantages, ERASL does have 3 drawbacks. Firstly, the processing time is increased significantly, as the laser has to move through an entire area to remove it, as opposed to a simple crosshatch pattern in the case of LOM. As a result, it was impractical to fabricate simple lattices beyond 2 unit cells x 2 unit cells x 2 unit cells or complex lattices beyond 1 unit cell for the present study (Fig. 2). The general insights drawn from our studies, however, are unlikely to be significantly impacted by a larger lattice size (Appendix A2). In fact, given that the mechanical properties of lattices may improve with more unit cells [22], there could be further room for improvement for PDACF properties, even though some of them have already exceeded those of current foams (Figs. 14 and 15).

Secondly, by burning off an entire area as opposed to cutting it out, more carbon is released back to the atmosphere, which is detrimental from an ecological standpoint. However, given that the demand would most likely lie with PDACFs with large relative densities (i.e. small amounts of material removed), which displayed the best mechanical properties (Fig. 12–15), this release of gaseous carbon from cellulose is expected to be rather limited.

Lastly, by eliminating cellulosic materials through laser-induced heating, the surface finish of the parts can be relatively rough, as it is difficult to control the spatial boundaries of the combustion process at a microscopic level. One way to potentially alleviate this might be to use a blade to trim the edges after printing. Since the current study is focused on the functional and structural properties of the PDACFs, however, surface finish is not as important a consideration and hence, no additional effort was made to polish the edges.

Notwithstanding the disadvantages of ERASL, it successfully realized anisotropic closed cell lattices for investigations for the first time. In the *Perpendicular* orientation, the moduli of PDACFs were found to be low but their elastic strain limits were high ($\sim 30\text{--}40\%$), allowing them to exhibit energy dissipation properties similar to graphene aerogels under cyclic loading. For comparison, conventional carbon foams usually suffer a catastrophic failure within 10% strain [13,17,30,67]. Despite

some expulsion of materials and the presence of fractures, *Perpendicular* PDACFs maintained their structural integrity after failure and were able to continue bearing load throughout. In contrast, *Parallel* PDACFs tend to delaminate into individual layers and lose their load-bearing properties upon failure at a relatively small strain ($\sim 5\text{--}10\%$), despite exhibiting a much stiffer modulus in the elastic regime.

An important factor contributing to these properties and failure processes is the alignment of the carbonized kraft fibers in PDACFs. In the *Perpendicular* orientation, the fibers were lying perpendicular to the load axis. Therefore, there was a much higher chance for the fibers to undergo bending deformation. Since the carbonized kraft fibers were very thin (thickness $\sim 1\text{ }\mu\text{m}$), they deflect easily and only a small load was required to compress the PDACF to a given strain, resulting in a low modulus. Consequently, the bending stresses sustained by the fibers are low, allowing the majority of the fibers to remain elastic up to relatively large compressive strains.

Conversely, in the *Parallel* orientation, a significant portion of the fibers were parallel to the load axis and subjected to axial loading, which tend to generate small strains despite large stresses, thereby conferring a relatively large modulus to the structures. The high stress levels sustained by the fibers, however, facilitated the initiation and propagation of fractures, which caused the structures to fail at small strains. Unfortunately, due to non-trivial challenges in obtaining micro-CT scans of PDACFs during mechanical testing, detailed experimental validation of the proposed microscopic deformation will have to be left to future studies.

Interestingly, the peak stress for both the *Perpendicular* and *Parallel* orientations was similar, even though *Perpendicular* PDACFs were observed to fail via fracture propagation through the layers, while *Parallel* PDACFs failed via fracture propagation between the paper-tape interface (i.e. delamination). This result suggests that there may have been a common physical mechanism behind the two different fracture paths. Indeed, a closer examination of the PDACF microstructure in Fig. 3 reveals that, regardless of the travel direction, failure onset would require microscopic fractures to initiate in and propagate through a multitude of fiber interfaces. Since the microstructural failure mechanism was similar, the strength in the different orientations was, consequently, comparable.

By combining the natural anisotropy in paper (fibers only lie in the plane of the paper sheet) with a macroscopic architecture that either enhances or suppresses the anisotropy, different properties can be obtained. For instance, excellent mechanical and energy absorption properties can be obtained with anisotropic honeycomb architectures. The specific energy absorption (SEA) normalizes the energy dissipated with the actual amount of material so that any difference in SEA can be attributed primarily to the microstructural arrangement of the material instead. Therefore, the unprecedented SEA – strength properties displayed by Honeycombs and Plate Simple Cubic PDACFs indicate that the hierarchical arrangement of loosely packed microscopic fibers within a broader architecture of anisotropic geometry is superior to the tetrakaidecahedron/ dodecahedron microstructure commonly observed in foams [60], as well as the cross-linked graphene platelet microstructures found in aerogels [20]. A large part of this can be attributed to the copious fiber interfaces present in the paper microstructure, which increased the fracture resistance of PDACFs, so that the fall from peak stress after failure was relatively gradual (Fig. 6), despite the brittleness of the individual carbonized fibers.

On the other hand, architecting PDACFs in the form of Plate Simple Cubic – Octet Truss or Plate Octet Truss can improve the isotropy of the

structure. This is clear from Fig. 12, which shows that the gap between the *Perpendicular* and *Parallel* moduli for these geometries bear smaller differences. Such isotropy could be useful for protective applications such as helmets and elbow pads, where the load can potentially come from a wide range of directions.

Furthermore, our results show that the carbonized cellulose and tape, which make up the PDACFs, were able to successfully function as an anode in a Li-ion battery for more than 300 cycles. Although the specific capacity of 65 mAh/g – 140 mAh/g fell short of the 350–370 mAh/g typically observed for graphite electrodes, it is similar to the capacity of commercial Lithium Manganese Oxide (LMO) batteries (~80–120 mAh/g) [73], indicating that PDACFs hold economic potential as a battery component. Moreover, the specific capacity is also within the range of that exhibited by pyrolyzed polymer foams [12], providing another avenue for carbonized cellulose to replace fossil fuels in the push towards the development of a “green” multifunctional structural material.

5. Conclusions

Carbon foams derived from pyrolyzed kraft paper and additively manufactured into closed cell, open cell and bulk structures through sheet lamination have been shown to be as stiff and strong as the best carbon foams produced through conventional means using non-renewable resources. These Paper-Derived Architected Carbon Foams (PDACFs) also exhibit significant elastic behavior up to 40% strain, with dissipative capabilities similar to that of aerogels. Certain Square Honeycombs and Plate Simple Cubic geometries, in particular, displayed a combination of compressive resilience, volumetric energy absorption, specific energy absorption and compressive strengths not found in current materials. Moreover, the kraft paper carbon foams were also found to exhibit stable specific capacities of 65–140 mAh/g, at a specific current of 10 mA/g, when used an electrode for Li-ion batteries. These structural and functional properties suggest that PDACF is a sustainable and scalable alternative to current porous carbon materials, and would find economic value in demanding, high-end, multifunctional applications, such as the nascent field of structural batteries.

CRedit authorship contribution statement

Chang Quan Lai: Conceptualization, Methodology, Formal analysis,

Data curation, Supervision, Writing – original draft, Writing – review & editing, Visualization, Funding acquisition, Resources. **Guo Yao Lim:** Investigation, Project administration, Methodology, Writing – review & editing. **Kai Jie Tai:** Investigation, Methodology. **Dominic Lim Kang Jueh:** Investigation, Methodology, Writing – review & editing. **Linghui Yu:** Methodology, Formal analysis, Resources, Writing – review & editing. **Pawan K. Kanaujia:** Investigation, Methodology. **Ian Seetoh:** Software, Formal analysis, Writing – review & editing, Visualization.

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.

Data availability

Data will be made available on request.

Acknowledgments

The authors declare no conflict of interest. This work was partially supported by Chang Quan Lai's startup grant (Funder: Nanyang Technological University, Singapore; Award No.: 020868-00001). We thank Prof. Jason Xu, for the loan of battery testing equipment, and Dr. Weiling Liu, for her help with the XRD measurements.

Data Availability

The data that supports the findings of this study are available within the article.

Appendix

A1. Pyrolysis of kraft paper

See Appendix Fig. A1.

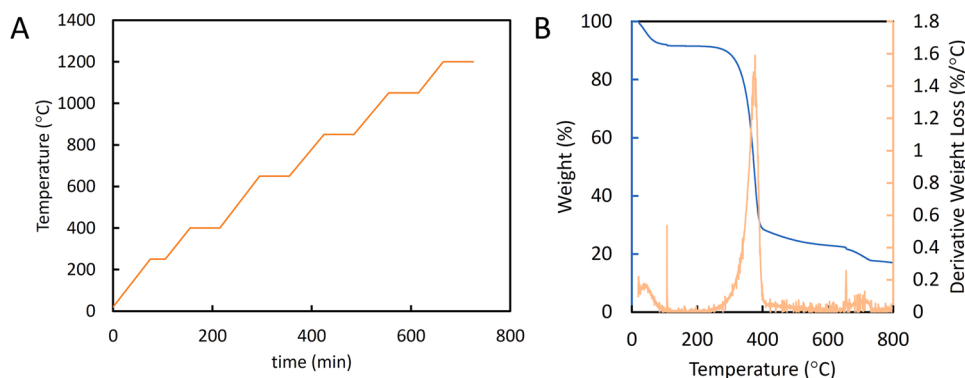


Fig. A1. (A) Temperature profile for pyrolysis of kraft paper. (B) Thermogravimetric analysis performed in TGA 2950 Thermogravimetric Analyzer (TA Instruments USA) at a fixed scan rate 10 °C/min in N₂. The sharp reduction in weight of the kraft paper at ~ 370 °C was also observed previously and is associated with the decomposition of glycosyl units to volatile products [38,74].

A2. Effect of large lattice size

See Appendix Fig. A2.

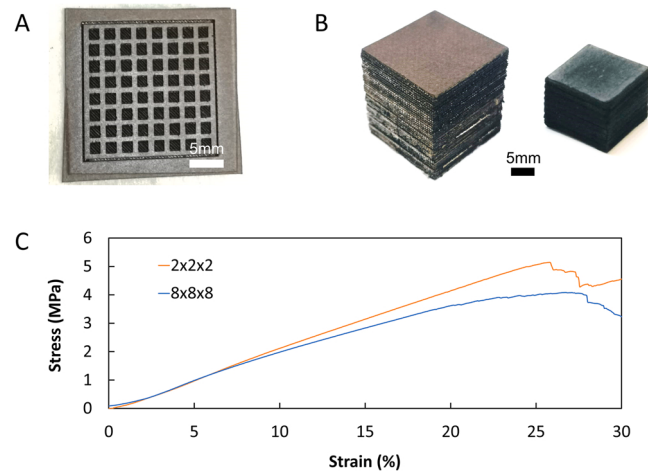


Fig. A2. (A) Image of an $8 \times 8 \times 8$ Plate Simple Cubic lattice being fabricated using ERASL (B) Image of the finished lattice and its pyrolyzed counterpart, showing no signs of shrinkage-induced warping. The slow area-removal process in ERASL renders such large lattices impractical to produce for the ~ 50 compressive tests conducted in this study. (C) Stress-strain responses of $2 \times 2 \times 2$ and $8 \times 8 \times 8$ Plate Simple Cubic PDACFs (relative density = 0.78) showing no significant deviation in modulus and peak stress despite the difference (64 times) in the number of unit cells.

A3. Properties of paper-derived architected carbon foams

See Appendix Table A1.

Table A1

Properties of the architected carbonized kraft paper structures. Skeletal density of the carbonized kraft paper, as measured by helium pycnometry, was 2.2 g/cm^3 . Lattice relative density can be obtained by normalizing the mass density against the PDACF cube density of $561.7 \pm 31.2 \text{ kg/m}^3$. Mass density of each geometry was determined by averaging the measurements for 2 different samples, one of which was used for testing in the Parallel orientation and the other in the Perpendicular orientation. Because the sheets used in this study had a thickness of 0.5 mm (i.e. z-axis resolution = 0.5 mm), the relative densities for each geometry were carefully selected so that the cavity height was in multiples of 0.5 mm to ensure faithful reproduction of the structures.

Orientation	Geometry	Density (kg/ m ³)	Young's Modulus (MPa)	Maximum Compressive Strength (MPa)	Maximum Energy Absorption Efficiency (%)	Specific Energy Absorption at Maximum Efficiency (MJ/m ³)
Perpendicular	Cube	547	36.7	13.30	32.4	4.312
		588	38.9	13.40	36.0	4.827
		528	34.8	11.40	31.2	3.550
		570	42.3	9.10	–	–
	Plate Simple Cubic	274	4.5	1.22	27.7	0.339
		351	18.5	2.73	32.3	0.882
		420	21.2	5.14	34.5	1.773
		193	5.1	0.18	27.0	0.050
	Plate Simple Cubic – Octet Truss	287	12.8	1.40	34.3	0.481
		346	24.9	1.81	26.5	0.479
		393	22.7	2.82	–	–
		393	22.3	2.83	27.2	0.770
	Plate Octet Truss	261	14.2	0.46	27.1	0.124
		267	17.0	0.96	21.5	0.205
		333	18.1	1.66	27.2	0.453
		159	5.3	0.78	32.1	0.251
Parallel	Triangle Honeycomb	332	22.3	3.40	36.7	1.248
		406	39.0	6.40	34.9	2.234
		298	23.3	5.40	32.5	1.754
		547	506.3	13.42	13.6	1.830
	Cube	588	531.6	13.52	15.0	2.024
		528	701.6	12.80	21.3	2.726
		274	95.5	2.92	18.7	0.547
		351	410.4	2.64	27.1	0.715
	Plate Simple Cubic	420	454.1	5.71	17.6	1.005
		193	31.3	0.17	12.5	0.022

(continued on next page)

Table A1 (continued)

Orientation	Geometry	Density (kg/m ³)	Young's Modulus (MPa)	Maximum Compressive Strength (MPa)	Maximum Energy Absorption Efficiency (%)	Specific Energy Absorption at Maximum Efficiency (MJ/m ³)
	Plate Simple Cubic – Octet Truss	287	104.6	0.96	24.9	0.239
		346	122.2	2.27	40.7	0.924
		346	204.5	2.56	–	–
		393	198.7	3.16	17.1	0.539
	Plate Octet Truss	266	36.0	0.52	7.5	0.039
		364	102.1	1.16	10.4	0.120
		444	113.9	1.78	19.1	0.341
		200	104.6	1.45	1.0	0.015
	Square Honeycomb	266	260.4	3.43	15.4	0.530
		364	291.3	6.70	15.1	1.014
		444	324.0	8.39	23.9	2.002

A4. Nitrogen adsorption-desorption isotherms

See Appendix Fig. A3, Fig. A4.

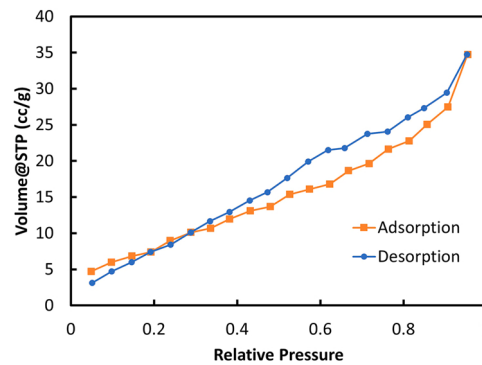


Fig. A3. Nitrogen adsorption - desorption isotherms for carbonized kraft paper.

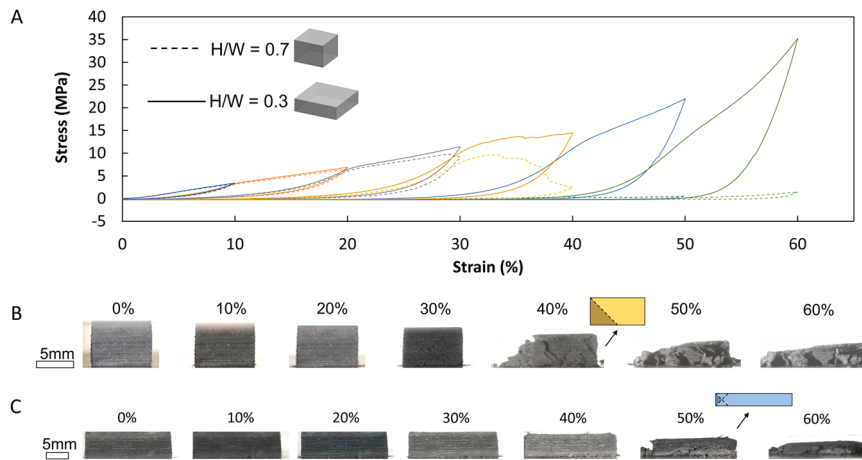


Fig. A4. (A) Cyclic loading stress – strain response of PDACF cuboids with height to width (H/W) ratios of 0.7 (dashed line) and 0.3 (solid line). Unloaded images of the PDACF cuboids with (B) $H/W = 0.7$ and (C) $H/W = 0.3$, after they have been compressed to the strain indicated above each image. Schematic diagrams in (B) and (C) illustrate the material segments (shaded regions) in the structures lost to fractures (dashed lines).

A5. Effect of aspect ratio on compressive resilience

A reduction in sample aspect ratio had been shown previously to improve the ductility of bulk metallic glass, which is normally brittle and fails catastrophically [75]. To extend the elastic strain limit for PDACF, the height to width ratio, H/W , of the cube structure was reduced from 0.7 (= 5.9 mm/ 8.2 mm) to 0.3 (= 5.9 mm/ 19.8 mm) to form a flat cuboid. Our results indicate that the modification did, indeed, increase the elastic recovery of PDACF to ~ 60% strain (solid line in

Fig. A3(A)). However, significant deviation began to appear between the unloading curve of the 50% strain cycle and loading curve of 60% strain cycle, a result of the extensive fractures that began forming after compression to 50% strain.

Based on photographic evidence and schematic illustrations in Fig. A3(B) and (C), it can be observed that this improvement happened because it prevented a substantial part of the structure from being lost to fractures that tend to propagate from the free outer edge at a ~ 45° angle [54]. In other words, a sample with higher aspect ratio (*i.e.* small width,

large thickness) will be more geometrically prone to losing a large volume of load-bearing material (shaded triangle in orange cuboid in Fig. A3(B)) than a flatter sample (blue schematic cuboid in Fig. A3(C)) due to the propagation of the same fracture. These observations are in line with the explanation provided for bulk metallic glass previously [75].

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