Strong, Fracture-Resistant Biomimetic Silicon Carbide Composites with Laminated Interwoven Nanoarchitectures Inspired by the Crustacean Exoskeleton


1. INTRODUCTION

Natural materials are distinguished by an exceptional efficiency in developing combinations of outstanding mechanical properties, e.g., strength and fracture toughness, using a limited selection of constituents.1–3 These materials, in particular their underlying design principles extracted from the perspective of materials science, offer a source of inspiration for the development of new, high-performance materials in man-made systems.4–8 In this regard, among the diversity of natural materials, crustacean exoskeletons are characterized by a unique multifunctionality to fulfill stringent mechanical tasks by providing not only mechanical support and load-bearing capability but also an effective protection to the body against environment and predators; some types of exoskeletons even function as a weapon for fighting or feeding.9 It has been well established that the mechanical performance of crustacean exoskeletons originates principally from their intricate structural design.10–21 A basic motif of such design is the nanoscale mineralized chitin-protein fibers that are arranged in a laminated fashion with their in-plane orientations continuously varying within the laminates, frequently forming twisted plywood or Bouligand-type architectures.12–13 This endows the crustacean exoskeletons with potent toughening mechanisms, specifically crack deflection/twisting and uncurred-ligament bridging, which results in increasing fracture resistance with crack extension, i.e., rising R-curve behavior, and outstanding strength–toughness combinations, especially as compared to layered composites. Our approach is feasible for the efficient fabrication of bioinspired composites mimicking crustacean exoskeletons and demonstrates a promising potential for the development of new synthetic lightweight structural materials with exceptional combinations of mechanical properties.

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composite plies, which contain unidirectionally aligned reinforcements but are rotated by different angles, followed by consolidation.\textsuperscript{22,24} This enables a precise control of the fiber orientations but generally results in a dimensionally coarse composite microstructure (typically on the length-scale of tens to hundreds of micrometers). Additive manufacturing, e.g., 3-D printing, allows for the construction of complex architectures in materials, thus providing a novel means for the fabrication of materials mimicking crustacean exoskeletons. The orientations of constituents with large aspect ratios can be readily regulated during processing by applying shear force or using magnetic or electric fields.\textsuperscript{5,8,25–29} However, this method is complicated by the necessity of surface modification of the constituents to make them magnetic- or electric-responsive using specific additives and an accurate modulation of applied fields in the process of manufacturing. Indeed, such “bottom-up” approaches, including layer-by-layer assembly, are generally restricted by a limited efficiency in fabricating bulk materials. Moreover, the materials reported to date that mimic crustacean exoskeletons using such methods invariably demonstrate poor interconnectivity both between the laminates and between the constituents within laminates. As such, these synthetic materials become susceptible to delamination and debonding of the fibers, which compromises their mechanical properties and can result in premature failure. In contrast, in natural crustacean exoskeletons, the adjacent fibers and laminates are interconnected or stitched together by abundant trans-lamellar tubules.\textsuperscript{10–14} Such interconnectivity represents an additional structural feature to be replicated in man-made materials mimicking crustacean exoskeletons.

2. RESULTS AND DISCUSSION

2.1. Structural Characteristics. Figure 1 illustrates the formation process of the bioinspired hybrid composites, which comprise freeze-cast silicon carbide containing a poly(methyl methacrylate) (PMMA) compliant phase and exhibit laminated interwoven nanoarchitectures that replicate the structural design of crustacean exoskeletons (as described in the Materials and Methods section). During the freezing process, a horizontal temperature gradient is generated in the slurry because of a polydimethylsiloxane (PDMS) wedge placed between the slurry and the cold finger, in addition to the vertical temperature gradient created by the cold finger. As such, the ice crystals nucleated at the bottom of the wedge preferentially grow in two directions, i.e., vertically from the bottom to the top away from the cold finger and horizontally along the wedge. This enables the ice crystals to grow into a long-range aligned lamellar structure.\textsuperscript{31,32} In this process, the nanoscale mineral particles and additives mixed in the slurry are gradually expelled into the microspace between growing ice crystals.\textsuperscript{33,34} In particular, the encapsulating force exerted by the moving ice front triggers the self-assembly of the silicon carbide whiskers, which possesses a large aspect ratio and anisotropy, by realigning their long axes preferentially parallel to the profile of growing ice crystals (Figure 1b).\textsuperscript{25,35} This leads to the laminated arrangement of whiskers with their in-plane orientations randomly distributed within the laminates. The subsequent sublimation of the ice via freeze-drying results in a scaffold with aligned pores replicating the ice crystals.

The pressing treatment along the orthogonal direction helps densify the scaffold to improve the mineral content in the composites. This plays an additional role in enhancing the
microstructural ordering of the composites by decreasing the out-of-plane misalignment of silicon carbide whiskers.36 In the sintering process, at a lower temperature than that used to sinter the silicon carbide, the scaffold is partially sintered with the silicon carbide whiskers interconnected by the doped silica nanoparticles (Figure 1c), resulting in a good integrity of the scaffold through the formation of abundant nanointerconnections in three-dimensional space. Additionally, this treatment produces mineral nanoasperities on the surface of whiskers, reminiscent of the nanoscale features of the mineral platelets in nacre.37−39 Such nanoasperities serve to promote bonding strength between the mineral and polymeric phases by increasing their interfacial roughness in biological and bioinspired materials.37−40 In the present composites, the interfaces can be additionally strengthened by grafting the scaffold with γ-MPS which creates covalent bonds between mineral reinforcements and PMMA matrix.41,42

Figure 2. Structure of sintered scaffolds and infiltrated composites compared to lobster exoskeleton and layered composites. (a) Structure of the exoskeleton of a lobster Homarus americanus [Adapted with permission from ref 10. Copyright 2005 Elsevier]. (b) Structures of layered composites with lamellar and dendritic morphologies [Adapted with permission from ref 42. Copyright 2015 Elsevier]. (c) SEM micrographs of the sintered scaffolds subjected to single and twice pressing treatment before sintering. (d) SEM micrographs of the polished cross sections of infiltrated composites with different mineral contents. SiCW41 and SiCW58 refer respectively to materials with mineral contents of 41 and 58 vol %. (e) XRT volume renderings of the composites with signal filtered for the silicon carbide reinforcements, i.e., the PMMA matrix is transparent.
regularity with their mineralized chitin-protein fibers aligned in a similar orientation within a single lamella.\(^\text{10−14}\) The lamellae may even display certain periodicity in their arrangement, sometimes forming the so-called Bouligand-type structure.\(^\text{11,12}\) In spite of the lack of a rigid replication of such characteristics per se, several underlying designs that essentially endow crustacean exoskeletons with exceptional biomechanical functionality have been successfully implemented in the present composites. This enables the activation of the principal mechanisms used by nature in the composites toward enhanced mechanical properties—it is through such an optimizing strategy in which the composites mimic the crustacean exoskeletons.

The porosity in the scaffolds can be adjusted by pressing the green bodies before sintering, leading to varying mineral contents in the resultant composites. Even lower mineral contents can be obtained without pressing and controlled by adjusting the concentration of mineral constituents in the slurry. The mineral contents of the present composites subjected to single and double pressing treatments were determined to be 41 vol % and 58 vol % (equivalent to \(\sim65\%\) and 79\% by weight), respectively. Such mineral contents are comparable to those of the natural lobster exoskeleton and the synthetic silicon carbide−PMMA composites with layered structures.\(^\text{19,42,43}\) Note here that the appearance of tiny pits in the scanning electron microscopy (SEM) images (Figure 2d) is an artifact caused by the pull-out of silicon carbide whiskers from the polymeric matrix during the polishing process of samples. No pores or apparent agglomeration of minerals can be detected in the XRT images (Figure 2e), indicating a complete infiltration and good structural uniformity of the composites.

### 2.2. Mechanical Properties.

The compressive stress−strain curves shown in Figure 3a demonstrate the capability of the composites to undergo large strains (exceeding 10\%) prior to fracture. In particular, the composites with lower mineral content (41 vol \%) display significant stable plastic deformation of over 20\% without apparent stress reduction. Both composites are much more ductile than monolithic silicon carbide which virtually has no plasticity. The compressive strength, hardness, and flexural strength are markedly improved with the increase of mineral content from 41 to 58 vol \% (Figure 3b). The work of fracture in bending, represented using the area under load−displacement curve divided by the area of the load-bearing cross-section of samples, presents an opposite varying trend with the composite with lower mineral content \(\sim73\%\) tougher than that with higher mineral content (Figure S1 in the Supporting Information for flexural stress−displacement curves). Moreover, the composites display strong mechanical anisotropy in hardness with the longitudinal orientation, i.e., the in-plane orientation of laminates, being significantly harder than the transverse orientation, i.e., the orientation orthogonal to laminates. Specifically, the hardness in the longitudinal orientation is \(\sim12\%\) and 27\%, respectively, higher than the transverse orientation in composites with mineral contents of 41 and 58 vol \% (hereinafter referred to as SiCw41 and SiCw58, respectively). The compressive strength demonstrates
a similar anisotropy in the SiCw41 composite; nevertheless, such a trend is insignificant for the SiCw58 composite (the decreased anisotropy may result from the presence of multiple randomly distributed nanointerconnections between the minerals as the compressive strength is largely associated with the failure of the scaffold of mineral reinforcements44). Tomography imaging reveals a distinct unevenness on the fracture surfaces of bent composites, as shown in Figure 3c, which contrasts to the smooth surfaces of monolithic PMMA or silicon carbide. This is presumed to result from the pull-out of whiskers or whisker bundles from the polymeric matrix and the shear deformation between laminates and acts to dissipate more mechanical energy at fracture. In addition, the cyclic compressive stress–strain curves of composites are characterized by remarkable hysteresis loops for both orientations (Figure 3d and e). This suggests a distinct capability for effective energy consumption by viscoelasticity during the loading–unloading cycles. The viscoelasticity is more prominent for the composite with lower mineral content (i.e., SiCw41) which exhibits stable hysteresis loops and large plastic deformation (Figure S2 in the Supporting Information for the amount of energy dissipation). Additionally, such composites demonstrate more efficient energy consumption for the longitudinal orientation, as compared to that in the transverse orientation.

The fracture toughness evaluation combined with in situ measurement of crack length by SEM observation reveals a rising crack-resistance (R-curve) behavior of the composites where the crack-growth toughness increases with crack extension (Figure 4a). Such stable crack growth contrasts to the catastrophic fracture of monolithic silicon carbide. Indeed, the main toughening function of compliant phase in ceramics is to stabilize slow crack growth to avoid sudden fracture. The composites with lower mineral content exhibit an improved crack-growth toughness in the form of a steeper R-curve and hence a higher tolerance for stable crack growth before instable fracture ensues. According to the ASTM standards (E1820-13), the maximum fracture toughness in terms of the J-integral of a specimen is limited by the smaller of \( \frac{b_0}{10} \) or \( \frac{B_0}{10} \) with \( \sigma_y \) being the effective yield strength; also, the maximum crack extension is limited by 0.25\( b_0 \). By applying such criteria, the critical valid fracture toughness was determined to be 1.0 ± 0.1 and 0.69 ± 0.07 kJ m\(^{-2}\), respectively, for the SiCw41 and SiCw58 composites, which is roughly 61% and 10% higher than that of monolithic silicon carbide. The impact toughness presents a similar varying trend with mineral content as the fracture toughness (Figure 4b). The SiCw41 and SiCw58 composites are, respectively, about 2.3 and 1.7 times tougher than monolithic silicon carbide under dynamic loading conditions.

It has been well-established that the layered arrangement of inorganic and organic constituents at the nano- to micro-length-scales in composites reminiscent of the designs in biological materials like nacre, generate several extrinsic toughening mechanisms, such as uncracked-ligament bridging, pull-out of crack bridges, and crack deflection along the interfaces.4,11,46−48 This may lead to a significant enhancement in the fracture toughness without necessarily decreasing...
strength, thus endowing the composites with superior strength–toughness combinations as compared to a simple mixture of constituents. Silicon carbide has been widely used as a reinforcement phase in strengthening the polymeric matrix in silicon carbide–polymer composite systems.\textsuperscript{25,49–52} The current hybrid materials are stronger than most of such polymer-based composites because of their higher mineral content and enhanced nanointerconnection between the reinforcements. In addition, the mechanical properties of the nacre-like silicon carbide–PMMA composites with layered structures have been investigated and correlated to their microstructural characteristics.\textsuperscript{42} These composites display a general varying trend of increasing strength and decreasing fracture toughness as the mineral content increases. Their mechanical properties are additionally associated with the composite architecture and can be improved by increasing the nanointerconnectivity between lamellae. A direct comparison shows that the present composites exhibit markedly higher fracture toughness than the layered ones at an equivalent level of strength (Figure 4c). Comparable strength–toughness combinations cannot be readily generated in layered composites without the presence of distinct interconnecting regions that can bridge the mineral lamellae.\textsuperscript{42} This demonstrates the marked efficiency of laminated interwoven nanoarchitectures in toughening natural composites, specifically as compared to the layered structures with lamellar or dendritic morphologies.

Reconstructed tomography imaging of crack propagation from a sharpened notch tip, shown in Figure 4d, reveals the existence of multiple mechanisms in the composites that serve to resist the growth of cracks. A prime feature is the tortuous nature of the cracking profile at the microscale. On the one hand, the crack displays a wavy path along its growth direction, resulting primarily from the laminated arrangement of constituents. Such in-plane crack deflection helps shield the crack tip from applied stress and is widely utilized as an effective toughening strategy in biological and bioinspired material-systems, especially those with layered structures.\textsuperscript{4,41,42,48} On the other hand, the inconsistency between the crack traces at differing longitudinal cross sections (slices 1–4) indicates apparent unevenness of cracking profile perpendicular to the growth direction. Such a characteristic, termed out-of-plane crack twisting to differentiate from the above-mentioned crack deflection, is clearly visualized in the through-thickness cross-section of XRT images (slice 5). Significant crack twisting has rarely been reported in layered composites in the case of cross-layer cracking, i.e., the crack propagates along the orthogonal direction of layered structure.\textsuperscript{4,42} This is due to the lack of microstructural heterogeneity in the composites along the out-of-plane directions. The enhanced crack twisting in the present composites is closely associated with the interwoven nanoarchitectures and the varying orientations of whiskers. It acts to increase the spatial complexity of the cracking profile and markedly strengthen the crack-tip shielding effect, thus allowing for more efficient toughening as compared to simple (in-plane) crack deflection.\textsuperscript{48}

Additionally, crack bridging is evident in our composites with the crack bridged by numerous nano- to microsized uncracked ligaments. In particular, the crack wake directly behind the crack tip remains largely intact and connected, as shown in the reconstructed images shown in Figure 4d. The fibrous nature of constituents and their good interconnection are responsible for the formation of numerous crack bridges; such bridges serve to inhibit the crack opening and carry load which would otherwise be used to promote crack growth. Their fracture and subsequent pull-out from the polymeric matrix additionally dissipate mechanical energy.\textsuperscript{53} Therefore, the outstanding mechanical properties of the present composites, in particular compared to those with layered structures, originate essentially from potent extrinsic toughening, principally in the form of enhanced crack twisting and uncracked-ligament bridging, which is generated by the implementation of the design principles derived from crustacean exoskeletons.

3. CONCLUSIONS

We have fabricated new silicon carbide hybrid composites containing a compliant phase with bioinspired interwoven nanoarchitectures mimicking crustacean exoskeletons primarily using a freeze-casting technique. The composites successfully replicate several basic design principles extracted from crustacean exoskeletons, i.e., the laminated structural arrangement, varying orientations of constituents, and three-dimensional nanointerconnections. This endows them with outstanding combinations of strength and fracture toughness for the silicon carbide–polymer material system, specifically as compared to the layered composites with lamellar or dendritic structural morphologies that mimic nacre. Our bioinspired composites exhibit improved toughness under both quasi-static and impact loading with rising R-curve behavior. In particular, the laminated interwoven nanoarchitectures demonstrate a remarkable toughening efficiency, especially as compared to the layered structures, by enhancing the extrinsic toughening primarily attained from in-plane crack deflection, out-of-plane crack twisting, and uncracked-ligament bridging. Our study offers a promising approach for an efficient fabrication of bulk hybrid materials that mimic crustacean exoskeletons using a “top-down” approach and for the preferential alignment of other constituents with large aspect ratios in composites. The enhanced combinations of strength and fracture toughness are critical for the structural applications of lightweight materials. We anticipate that the current composites may be potentially used to partially replace PMMA or other polymers in areas where higher strength is needed, or to partially replace ceramic materials where improved toughness is preferred. Additionally, the current design motifs inspired by crustacean exoskeletons may be further employed to develop new nanocomposites with exceptional mechanical properties, especially in toughening materials that are inherently brittle.

4. MATERIALS AND METHODS

4.1. Composite Fabrication. The processing route used to fabricate the nanocomposites is illustrated in Figure 1. An aqueous suspension was prepared by dispersing in deionized water 11.2 wt % silicon carbide whiskers (in β-crystalline form, Ksfuns Co., China), with diameter of 0.1–1 μm and length of 5–10 μm, 0.4 wt % silica nanopowders (Huisheng New Materials Co., China), with diameter of ∼15 nm, and 0.2 wt % Darvan CN dispersing agent (R.T. Vanderbilt Co., Norwalk, CT). The viscosity of the slurry was adjusted by adding 1.6 wt % hydroxypropyl methylcellulose (Meryer Co., China), 3.9 wt % poly(vinyl alcohol) (molecular weight of 84–89 kDa, Meryer Co., China), and 3.9 wt % sucrose to avoid gravitational sedimentation. These organics also serve as a binder of mineral powders after removal of the water. The mixture was ball-milled for 24 h, desired by adding one drop of defoamer (XP-M-120, Huaxing Co., China), and then
The samples were sputtered-coated with a electron microscope operating at an accelerating voltage of 20 kV.

The content of the mineral phase. Energy dispersive spectroscopy dimensions as those used for uniaxial compression were loaded and the range of 10 to 20 °C/min based on its freezing front velocity. Frozen samples were dried in vacuum below 5 Pa for over 48 h using a Scientz-10ND freeze drier (Scientz Biotechnology Co., China). These samples were subsequently pressed at 65 MPa along the orthogonal direction of the lamellar structure at ~130 °C, the softening temperature range of the organics. The green bodies were heat-treated at 500 °C for 2.5 h in air to burn out the organics and then sintered at 1100 °C for 2 h. This sintering temperature was chosen to limit oxidation of the silicon carbide while still allowing the nanometer-sized silica to be sintered to form nanointerconnections.

The green bodies were additionally densified before sintering by subjecting them to a pressure of 65 MPa along the orthogonal direction to generate a higher mineral content in the final composites. The as-sintered scaffolds were grafted with γ-methacryloxypropyltrimethoxysilane (γ-MPS, Chiyechem Co., China) by immersing in a methanol–water solution (methanol/water = 9/1 by weight) containing 20 wt % γ-MPS for 24 h. The pH of the solution was adjusted to 4 by adding acetic acid before immersing. Such surface modification helps strengthen the interfacial adhesion between the mineral and polymeric phases after infiltration. The grafted scaffolds were dried at 50 °C for 10 h and then infiltrated with methyl methacrylate (Jihua Co., China) containing 0.5 wt % 2,2-azobisisobutyronitrile as an initiator under a negative pressure below 80 kPa. The samples were heat-treated at 40 °C for 40 h and additionally at 90 °C for another 2 h to allow for a full polymerization of the monomers to form the PMMA matrix in the composites.

4.2. Characterization. Scanning electron microscopy imaging was performed on the sintered scaffolds and polished cross sections of infiltrated composites using a LEO Supra-55 field-emission scanning electron microscope operating at an accelerating voltage of 20 kV. The samples were sputtered-coated with a film of gold before imaging. Energy dispersive spectroscopy measurement was carried out using an Oxford Model 7426 spectrometer. X-ray tomography imaging was performed using an Xradia VersaXRM-500 3D X-ray microscope operating at an accelerating voltage of 80 kV. Images were processed and analyzed using the Avizo Fire 7.1 software.

Hardness measurements were conducted on the polished profiles of composites using an MH-5L Vickers hardness tester with a load of 1 kg and dwell time of 15 s. Uniaxial compression tests were performed on rectangular samples with a cross-section of 2 mm × 2 mm and height of 4 mm at a strain rate of 10−3 s−1 using an Instron 5982 testing system equipped with an Instron 2580 static load cell and an Instron 2601-92 linear variable differential transformer deflection sensor. For cyclic compression, samples with the same dimensions as those used for uniaxial compression were loaded and unloaded repeatedly at a constant strain rate of 10−3 s−1 to reach a constant increase of strain of ~1% at each cycle until failure. Flexural tests were performed on beam samples cut and polished to a cross-section of 2 mm × 1.5 mm with a loading span of 20 mm, in accordance with ASTM Standard C1161-13. The tests were carried out at a displacement rate of 0.06 mm min−1 using an Instron E1000 testing system with an Instron 2527-302 load cell and an accessional displacement sensor. After testing, the fracture surfaces of samples were examined using an Olympus LEXT OLS-4000 3D measuring laser microscope. Impact tests were conducted on samples with the same dimensions as used for the flexure tests, using a Zwick−Pendulum impact testing machine with impact energy of 2 J. The bending and impact mechanical properties of composites were measured as a function of applied load along the orthogonal direction of the laminates. This is the most common loading direction for static or impact bending in terms of the application of laminated composites in both natural (e.g., crustacean exoskeletons) and man-made systems. At least four samples were tested for each type of mechanical test. The differences in mechanical properties were tested using two-tailed Student’s t-test with values P < 0.05 being considered statistically significant.

Single-edge notched bend SE(B) tests were performed on samples cut and polished to a width (W) of 3 mm and thickness (B) of 1.5 mm with a loading span of 12.5 mm. The samples were side-notched to a depth of ~1.5 mm perpendicular to the plane of whisker alignment using a low-speed diamond saw with the notch root sharpened by a razor blade, in general accordance with ASTM designation D5045-99. In this configuration, crack propagation was aligned to be nominally perpendicular to the laminates, i.e., in the direction that toughening from fiber pull-out and crack bridging is most active. Testing was conducted at a displacement rate of 4 × 10−3 mm min−1 on a JEOL MicroTest stage inside the chamber of a JEOL JSM-6510 scanning electron microscope. Nonlinear-elastic fracture mechanics methods were employed to evaluate the fracture resistance of the composites in terms of the J-integral as a function of crack extension, Δa. J is defined as the rate of change in potential energy per unit increase in crack area for a nonlinear elastic solid; the critical value of J, e.g., at crack initiation or for crack growth, can be equated to the fracture toughness of the material. The J-integral, corresponding to each crack length, a, which was measured in situ in the SEM, is given by J = (1.9A∞)/Bh, where A∞ is the total area under the load–displacement curve and b is the uncracked ligament width (i.e., b = W − a). More details about the analysis can be found in refs 41 and 42.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsanm.9b00063.

Compressive strength, flexural stress–displacement curves, and energy dissipation during the loading–unloading cycles for cyclic compression of the hybrid composites with laminated interwoven nanoarchitectures inspired by the crustacean exoskeleton (PDF)

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### Notes

The authors declare no competing financial interest.

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