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Mechanical properties and toughening mechanisms of natural silkworm silks and their composites

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A R T I C L E I N F O

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A B S T R A C T :

There is an emerging interest in natural silkworm silks as alternative reinforcement for engineering composites. Here, we summarize the research on two common silkworm silks and silk fibre reinforced plastics (SFRPs) from the authors over the past few years in the context of related research. Silk fibres from silkworms display good strength and toughness under ambient and cryogenic conditions owing to their elastic-plastic deformation mechanism. In particular, the wild *Antheraea pernyi* (*A. pernyi*) silk also displays micro- and nano-fibrillation as an important mechanism for toughness and impact resistance. For SFRP composites, we found: (i) it is critical to achieve silk fibre volume fraction to above 50% for an optimal reinforcement and toughening effect; (ii) the tougher *A. pernyi* silks present a better reinforcement and toughening agent than *B. mori* silks; (iii) impact and toughness properties are advantageous properties of SFRPs; (iv) hybridization of natural silk with other fibres can further improve the mechanical performance and economics of SFRPs for engineering applications; and (v) the lightweight structure designs can improve the service efficiency of SFRPs for energy absorption. The understanding on the comprehensive mechanical properties and the toughening mechanisms of silks and silk fibre-reinforced polymer composites (SFRPs) could provide key insights into material design and applications.

1. Introduction

Natural silks are well recognized with a balance of light-weight, strength, extensibility and toughness (Shao and Vollrath, 2002; Keten et al., 2010; Vepari and Kaplan, 2007). Like most natural materials, such as nacre, hair and bone, the outstanding performance of silk primarily stems from its multi-layer structure and hierarchical architecture (Wortmann et al., 1997; Yu et al., 2016; Wegst et al., 2014; Munch et al., 2008). Natural silkworm silks are versatile (Malay et al., 2016), among which the most widely studied silk species is the mulberry silk from the silkworm *Bombyx mori* (*B. mori*) and the representative non-mulberry silk from the silkworm *Anthearea pernyi* (*A. pernyi*). In China, there is an annual production of ~680,000 tons of *B. mori* cocoons (~80% of the global production) (Qian et al., 2019), which mainly flows to the textile industry around the world. As the R&D interest on reconstituted silk fibroin for biomaterials increases dramatically over the past decades, the applications of silk fibres find more opportunities. Nevertheless, as the Queen of textiles prior to the emergence of synthetic counterparts, silks have not been explored much in reinforcing/toughening composites, especially with synthetic matrix polymers.

In the following, we provide a research summary on the structure characteristics and mechanical properties of two silkworm silks and corresponding SFRPs based on works from our team and collaborators. First of all, understanding the molecular structures of natural silkworm silks and cocoons is critical toward the optimal design and application of SFRPs (Guan et al., 2017).

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For the development of SFRPs utilizing natural fibres to optimize toughness, the following aspects are discussed. Firstly, what is the effect of fibre volume fraction (V_f) on the mechanical properties of SFRPs? Secondly, what is the reinforcing difference between the two silk species? Thirdly, is there any composite property that highlights the structure and property characteristics of silk? Fourthly, is there a way to improve/further expand the stiffness and strength of SFRPs for standard engineering applications? Furthermore, can lightweight designs be introduced to SFRPs for improved energy absorption? We address these questions in the context of related research in this paper, and hope to provide some insights on the design and processing of natural silk reinforced composites for future research.

2. Toughening mechanisms in natural silkworm silks and cocoons

The multi-scale toughening mechanisms in natural silks have been a focused topic of interest in the field of natural fibres (Niu et al., 2018; Fu et al., 2011; Liu et al., 2008). However, the majority of the research has addressed the strongest and toughest spider silks (Liu et al., 2008; Kubik, 2010). Given that all the naturally spun silks share certain structure characteristics, we try here to illustrate the structure of silkworm silks and compare them with spider silks.

At the primary structural scale of amino acid sequence, the heavy chain of *B. mori* silks contains a highly repetitive motif GAGAGS, whereas *A. pernyi* silk contains $[A]_n$ and GGX motifs, similar to *Nephila* spider dragline silk (Kubik, 2010). The GGX motifs with G = Glycine, X = typically Alanine/Serine/Tyrosine/D-Aspartic acid/Lysine/Arginine are thought to form spring-like helical conformations, which could contribute to the extensibility in the mechanical performance (Nguyen et al., 2015). At the secondary structure scale, most silks contain multiple conformations, and quantitatively resolving their composition has been obtained using various characterization techniques (Hu et al., 2006; Monti et al., 2001). *B. mori* silk contains ~50%–60% β-sheet conformation (Drummy et al., 2007), whereas *A. pernyi* silk contains ~40% β-sheet conformation. For the condensed structure, a number of models have been proposed, including the "string of beads" model (each bead consisting of β-sheet type folds) (Porter and Vollrath, 2009), the "fringe-micelle" model (the fringe represents the ordered β-sheet conformation and the micelle represents the disordered conformations) (Hagn et al., 2010; Lin et al., 2009) and the semi-crystalline model (β-sheet crystallites are embedded in the matrix of other conformations) (Termonia, 1994; Gosline et al., 1986). At a larger length scale, most silks are believed to consist of sub-micron fibrils. It is noted that *B. mori* silk lacks submicron fibrillar structures due to the high crystallinity and extensive physical cross-links in the fibre. At the macro-structure level, silkworm silks constitute a cocoon composite by bonding with sericin.

The mechanical behaviour of *B. mori* and *A. pernyi* silks is studied in detail in the works of Fu et al., 2011; Guan et al., 2012. The three main ways to acquire the silk fibre are laboratory processed from cocoons (with/without sericin coating), forcibly reeled from silkworms (with sericin coating) and industry processed textile reels/fabrics (without sericin coating). Because the industry processing of silk involves alkali solution, heat and mechanical stretching treatments, the mechanical behaviour of textile silks are affected (often negatively) and the mechanical property indexes, *i.e.* tensile strength and elongation, are lower

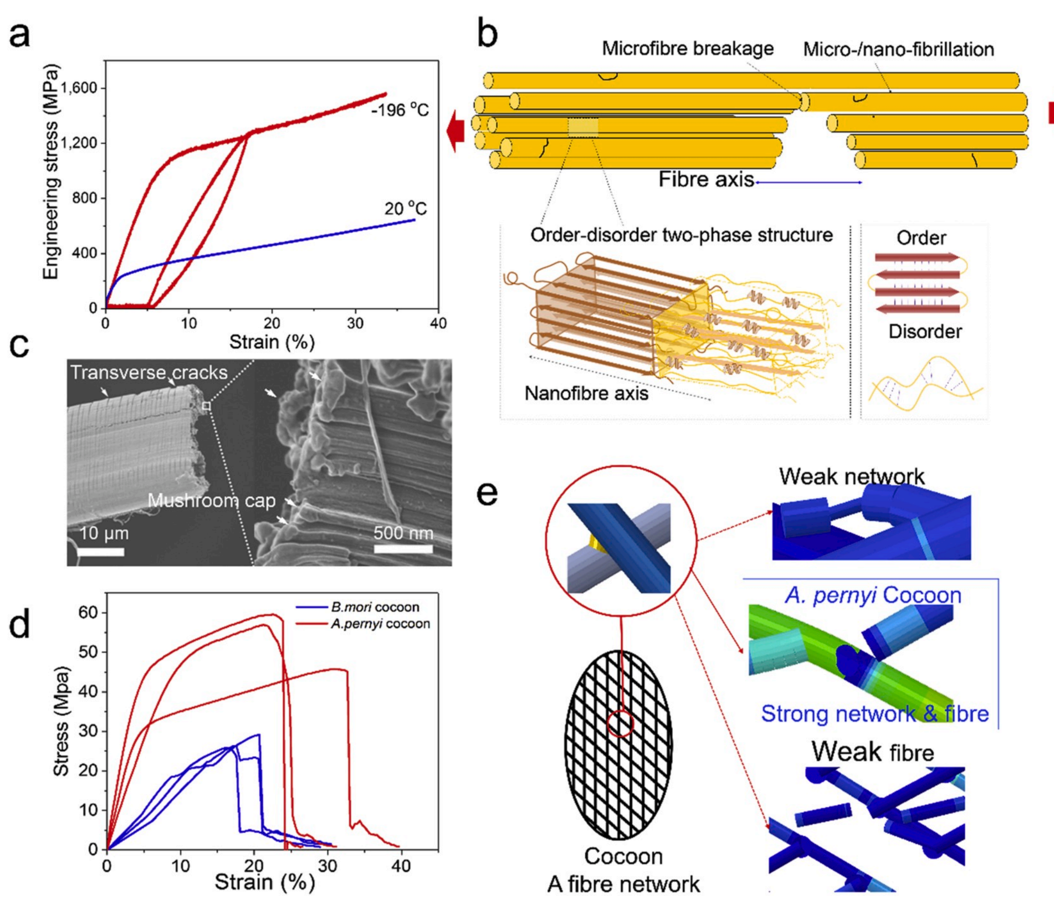

Fig. 1. Mechanical behaviour and toughening mechanisms in natural silkworm silk and cocoon. (a) Tensile stress–strain curves of *A. pernyi* filament at room temperature and at -196 °C. (b) Schematic of the hierarchical structure of *A. pernyi* silk fibre and toughening mechanisms at various structural levels. (c) Fractured end of a silk fibre broken at -196 °C. (d) Tensile stress–strain curves of *B. mori* and *A. pernyi* cocoons. (e) Finite element model simplification of tensile fracture modes in silk cocoon composites. Reproduced with permission (Guan et al., 2017). Copyright 2017, Elsevier.

than the laboratory processed silks (Yang et al., 2019a).

Our recent work (Fu et al., 2019) revealed that *A. pernyi* silk, forcibly reeled from silkworms, exhibits superior cryogenic ductility, and a breaking strain as high as ~31% at -196 °C. The breaking energy doubled from 154 MJ m^{-3} at room temperature to 339 MJ m^{-3} at -196 °C, as shown in Fig. 1a.

Multi-scale toughening mechanisms relating to molecular structure and morphology are believed responsible for the cryogenic ductility of *A. pernyi* silk, as outlined in Fig. 1b. Nano-fibrillation (refer to the Cook-Gordon theory (Raab, 1995; Raab et al., 1993)), together with micro-fibre breakage and dissociation, contributes to the energy absorption and dissipation. It is proposed that the nano-fibrillation mechanism is temperature-independent and can be activated with minimal energy. At the molecular level, *A. pernyi* silk contains an order–disorder two-phase structure rendering the elastic-plastic deformation. In Fig. 1c, the "Mushroom cap'' fracture-ends of nano-filaments demonstrated the elastic-plastic deformation mechanism in this silk.

As natural silk composite, cocoons consist of 3D woven silk fibre and a binder sericin glue. They act as a damage-tolerant protective shelter for silkworm pupae against impact and puncture damage (Chen et al., 2010, 2012). The sericin glue, which was traditionally discarded, was discovered to effectively bind sheets in biocomposites (Morin and Alam, 2016). In our previous work (Guan et al., 2017), the domestic *B. mori* cocoon and a representative wild *A. pernyi* cocoon were compared to reveal the structure and mechanical property differences in natural silk composites. In Fig. 1d, *A. pernyi* cocoons exhibit approximately a two-fold higher tensile strength (at 55 MPa) and 56% higher elongation (at 25%) than that of *B. mori* cocoons. Clearly, *A. pernyi* cocoons are a stronger and tougher material than *B. mori* cocoons. Using a finitel element model in Fig. 1e, we showed that the stronger fibre bonding in *A. pernyi* cocoons ensured effective stress transfer among the fibres. Simultaneously, *A. pernyi* silk's greater toughness contributed to the superior toughness of the *A. pernyi* cocoons. By improving the connections between fibres in *B. mori* cocoons, the cocoon mechanical performance could be vastly improved (Wang et al., 2017). Such new insights could guide the design and fabrication of composites based on natural fibres for unprecedented mechanical properties.

3. Mechanical properties and toughening mechanisms in SFRPs

Silk fibres from silkworms display good strength and excellent toughness (as shown above), and biodegradability as well as biocompatibility (Shah et al., 2014a). There have been efforts to study silk fibres as reinforcements for polymers, especially biopolymers (Shah et al., 2014a; Smitthipong et al., 2016; Eshkoor et al., 2013a, 2013b; Ho et al., 2011). Silk proved to be an effective toughening component for brittle glassy polymers (Ude et al., 2014; Shah et al., 2014b). Generally, two categories of silk composites have been investigated: short/chopped silk fibre reinforced thermoplastics and continuous/woven silk fibre reinforced thermosets (Shubhra et al., 2011; Zhao et al., 2016a; Cheung et al., 2010). Silk nanofibers and short fibers were usually used in composites for biomedical applications (Cheung et al., 2010; Li et al., 2008), whereas continuous silks and woven fabrics have been proposed as a toughening agent for thermoset polymer or glassy polymer matrices for impact-critical applications (Shah et al., 2014b). The effects of fibre content, fibre length, fibre modification and manufacturing method on their mechanical properties have also been explored (Li et al., 2008, 2019; Shubhra and Alam, 2011; Sekhar et al., 2012; Ho and Lau, 2012; Mazumder et al., 2019; Zhao et al., 2016b). Here we focus on composites reinforced by continuous silk/ woven silk fabric (Yang et al., 2016).

Firstly, the effect of silk fibre volume fraction (V_f) is discussed. *B. mori* silk fibre reinforced epoxy resin composites (*Bm*-SFRP) were prepared with V_f ranging from 30% to 70% via manual lay-up and hot-press under 0.3MPa pressure. Below $V_f = 50\%$, most mechanical properties, *i.e.* the tensile and flexural modulus, of SFRPs increased linearly with increasing V_f. However, when $V_f > 50\%$, a steep increase in the impact strength of SFRPs was observed, and the impact-resistance of silk fibres was dominant (Yang et al., 2016). Most importantly, *Bm*-SFRPs were able to achieve a V_f as high as 70%, owing to the tight woven fabric structure and greater compressibility of *Bm* silks compared to discontinuous plant based fibres. Shah and Vollrath discussed the potential opportunities of silks as an alternative reinforcement to plant fibres such as flax, and stressed that the attributes of textile silk fibre, such as compressibility, should be a great bonus for SFRPs (Shah et al., 2014b; Faruk et al., 2012). It is interesting that *Bm*-SFRP ($V_f = 60$ vol%) showed the best flexural strength and impact strength. We propose that a sufficient volume fraction of the matrix polymer is also required for flexural and impact properties of SFRPs, and it is critical to achieve silk fibre volume fractions above 50% for an optimal reinforcement and toughening effect.

Secondly, we found that the tougher *A. pernyi* silks provide an improved reinforcement and toughening agent than *B. mori* silks. In an earlier work (Yang et al., 2017), *A. pernyi* silk fibre reinforced composites (*Ap*-SFRPs) were prepared and compared with *Bm*-SFRPs. *Ap*-SFRPs with $V_f = 60\%$ exhibited a 100% improvement in tensile strength, 200% increased flexural strength and one order of magnitude higher breaking energy (11.7 MJ m^{-3}) compared to the pristine matrix. Specifically, the *Ap*-SFRP remained ductile and tough with 7% flexural strain and 24.3 MJ m^{-3} flexural breaking energy at -50 °C, as shown in Fig. 2a. As discussed earlier, mechanisms included molecular relaxations in the helical conformation structure and the slippages/splitting in micro- and nano-fibrillation during the deformation; these contributed significantly to the superior toughness of the *A. pernyi* silk fibres, compared to *B. mori* fibres, which resulted in the greater toughness of the *Ap*-SFRPs.

Thirdly, we propose that impact and toughness properties are the focal and advantageous properties of SFRPs. It was shown that natural silk fibres under quasi-static and dynamic rates exhibited considerable breaking energy absorption (Mortimer et al., 2014; Drodge et al., 2012). In Charpy impact testing, *Ap*-SFRPs ($V_f = 60\%$) showed significantly improved impact strength (>100 kJ m^{-2}) with ductility indexes (DI = $E_p/E_i = 3.88$) compared to *Bm*-SFRPs and pure carbon fibre-reinforced composite (CFRP) with the same matrix (Fig. 2b and c). Delayed fracture coupled with plastic deformation in these SFRPs provide multiple contributions to the dissipation of impact energy (Fig. 2d). Specifically, the greater deformation capacity of the *A. pernyi* silk fibres provides more possibilities for interfacial de-bonding and fibre pull-out. Unlike brittle FRPs which avoid interface failure, distributed microcracks on the silk-epoxy resin interface and fibre shear against the epoxy resin, initiated by such interfacial cracking, are considered important energy absorbing/dissipation mechanisms in SFRPs under impact. As a proof of concept, the crashworthiness and fracture toughness of composite structures from SFRPs were found to be excellent (Ude et al., 2014; Shah et al., 2014b).

Here the question may arise, can we estimate the mechanical properties of SFRPs from the mechanical properties of the components, silk fibre and the polymer matrix? The rule of mixture is a simple rule to estimate composite properties (Liu, 1997). The challenge of applying the rule of mixture to SFRPs is the nonlinear stress-strain behavior of silk fibres. Moreover, the textile processing and the woven fabric structure also influence the mechanical properties of SFRPs. We found that the properties of single fibres taken from the fabric appeared even lower than the final composites. For example, the mean tensile modulus of *B. mori* silk fibres was only 5.8 GPa, lower than the 7.8GPa for *Bm*-SFRPs ($V_f = 50\%$) (Yang et al., 2016). A further challenge also lies in the prediction of the interface properties, which is critical for coherent composite mechanical performance. An investigation on predicting the mechanical properties of SFRPs using modelling is undergoing.

As mentioned above, the interface properties between silk fibre and polymer matrix are important for mechanical property prediction of the composite. The silk-epoxy resin interface strength was quantified using interface shear strength (ILSS) with a value of ~20–40 MPa. Accordingly, to improve the interface strength, several strategies can be

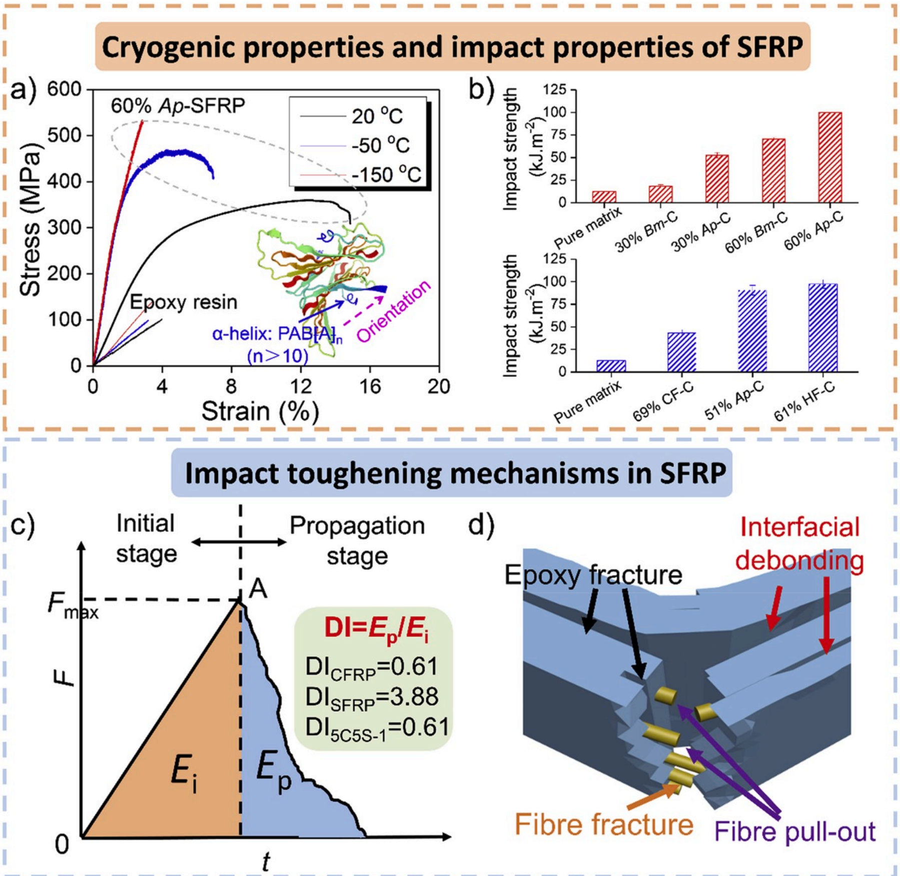

Fig. 2. Mechanical properties and toughening mechanisms in SFRPs. (a) Flexural properties of pristine epoxy resin and *A. pernyi*-SFRPs at sub-ambient temperatures. The molecular structure of *A. pernyi* silk is inserted. (b) Impact strength of SFRPs from two silks at various fibre volume fractions V_f. (c) Schematic force–time curve and measured DI in Charpy impact test. (d) Schematic of impact fracture behavior and associated energy absorbing/dissipation mechanisms. E_i: Energy absorption in initial elastic deformation; E_p: Energy absorption in plastic deformation. DI_{CFRP}, DI_{SFRP} and $DI_{5C5S\text{-}1}$ represent the ductility indexes of CFRP, SFRP and 5C5S-1. *Bm*-C, *Ap*-C and HF-C represent the *B. mori, A. pernyi* silk and hybrid fibre reinforced epoxy resin composites.

applied, including the exposure of more functional groups from silk fibre, and the application of appropriate multifunctional agents to bond the silk with the matrix. Earlier surface modification methods (Yang et al., 2019b; Ye et al., 2019; Yuan et al., 2010), such as crystalline/ordered structure dissolution using hexafluoroisopropanol/HFIP to expose more functional groups, were shown to result in a stronger interface in SFRPs. We also investigated the molecular interactions between the silk fibroin and the epoxy resin matrix polymer (Yang et al., 2019b). The results showed the T_g (Glass transition temperature) of reconstituted silk fibroin shifted when mixed with epoxy resin in the composite film. This indicated that silk fibroin polymers could react chemically via amine/hydroxyl-epoxy reactions, and also interact physically with epoxy compounds to affect the segmental chain motions at the nanoscale. Nevertheless, silk fibroin in silk fibers are in a highly ordered conformation and structure. Therefore, to improve the interface adhesion in SFRPs, the condensed structure on the silk fibre surface can be modified. Addtionally, a coupling agent between silk and epoxy resin matrix, alike the sizing agent for carbon fibre, needs to be developed in order to fulfill the mechanical strengths of silk in particular the toughness.

4. Hybridization and lattice structure designs for SFRP

Natural silk fibre reinforced composites display excellent toughness properties, but are there ways to further enhance the stiffness and strength of SFRPs? Hybridization design is a common strategy in FRPs to achieve balanced mechanical properties, environmental resistance and economics. To address the fourth question in the introduction, we adopted two fibres (carbon fibre/flax fibre) for hybrid fibre reinforced composites (HFRPs) to modulate the mechanical properties of silk-based composites (Yang et al., 2019a; Wu et al., 2019).

Comprehensive radar plots for the two series of hybrid fibre composites (HFRPs) are shown in Fig. 3a,c. Inter-layer and intra-layer hybridization, hybrid ratio and layer configuration were varied to tune the mechanical properties. Basic tensile/flexural strength and stiffness of HFRPs followed a trend of a linear increase with increasing hybrid fibre content. The combination of carbon and flax fibres can effectively enhance the stiffness (elastic modulus) of silk composites, making SFRPs more competitive with other structural engineering materials. For example, the addition of carbon fibres significantly improves the creep resistance and moisture sensitivity (Yang et al., 2019a). For HFRPs manufactured with both carbon and silk fibres, alternate stacking of the hybridized fibres leads to composites with much higher impact strength (98 kJ m^{-2}) than those composites manufactured from pure carbon fibres. Therefore, hybridized silk fibre reinforcements have been proposed as a remedy for the brittle fracture behavior of many carbon-fibre reinforced plastics (CFRPs) under impact loading (Li et al., 2013; An et al., 2012). For flax and silk fibre HFRPs manufactured from flax fibre and silk, the stiffening effect was clearly in evidence with the addition of the flax fibres; correspondingly, the addition of silk fibres was found to minimize the impact damage during drop weight tests. Nevertheless, SFRPs manufactured from pure silk fibres, especially *Ap*-SFRPs, displayed the best impact properties, as compared to HFRPs and CFRPs. Similar to the estimation of mechanical properties of SFRPs from those of silk and matrix, the forecast of the mechanical properties of HFRPs was expected based on the strength model in previous literature (Zhang et al., 2012), but this needs to incorporate modifications because of the nonlinear behavior of silk. This work is undergoing in our team.

An important benefit of silk fibres is their relatively low density (1.3 g cm^{-3}), which naturally serves to enhance their specific mechanical properties. Fig. 3b further compares the impact strength of silk-carbon HFRPs taken from our own studies and previous works (Yang et al.,

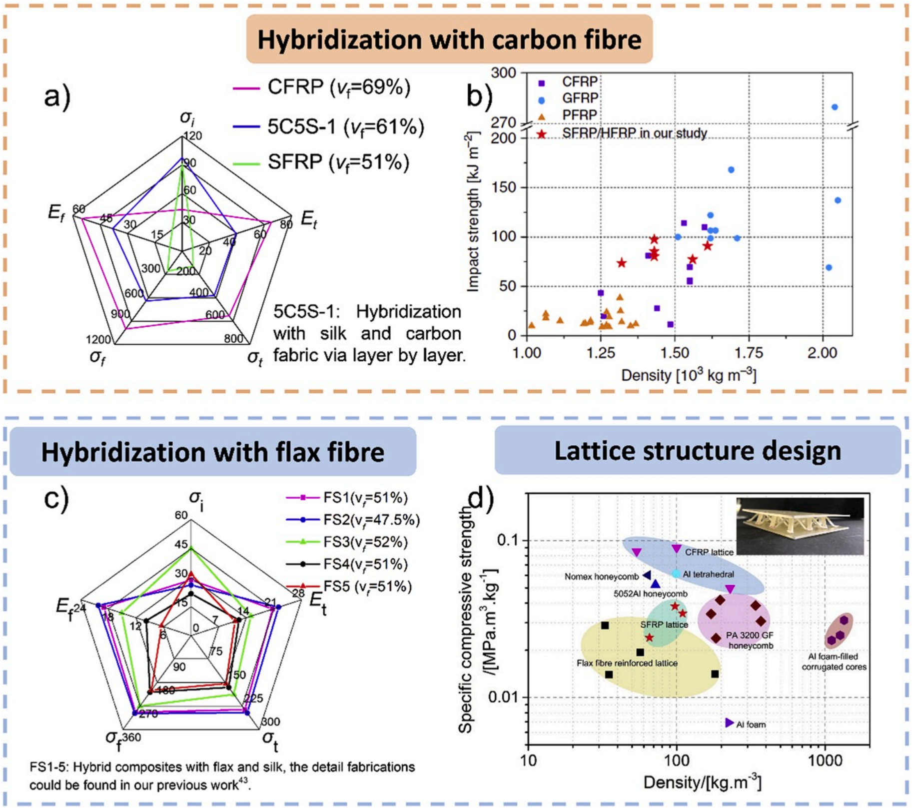

Fig. 3. Evaluation of the comprehensive mechanical properties in HFRPs and SFRP with lattice structure. Comparative radar plots of the key mechanical properties of silk-carbon HFRPs (a) and silk-flax HFRPs (c). (b) Comparison of impact strength versus density of silk-carbon HFRPs. (d) Ashby plot of compressive strength-density for foams/lattice structures and other solid materials. Key and units: Impact strength σ_i (kJ.m^{-2}), tensile modulus E_t (GPa), tensile strength σ_t (MPa), flexural modulus E_f (GPa), flexural strength σ_f (MPa). Adapted with permission (Wen et al., 2019). Copyright 2019, Wiley-VCH.

2019a). Both SFRPs and HFRPs can be seen to exhibit excellent specific impact properties in a density range of 1.3–1.8 g cm^{-3}. To briefly conclude, hybridization of natural silk with a high-performance synthetic fibre, such as carbon fibres, can render silk-based composites stiffer, stronger, creep- and moisture-resistant for engineering applications; furthermore, hybridization of silk with low-cost natural plant fibres, such as flax fibres, can make silk-based composites stiffer, stronger and more economically viable.

Lattice and sandwich structures are important designs for structural materials to achieve both light weight and superior mechanical performance. As demonstrated above, SFRPs and silk-based HFRPs displayed high toughness and energy absorption capacity. Here to address the final question for the development of SFRPs, we designed and manufactured lightweight silk lattice structures (SCLs) with pyramidal cores (Wen et al., 2019). Unidirectional silk-epoxy resin prepregs were prepared and stacked layer by layer in the lattice structure to create strong connections in the joints of struts. We note that silk yarns appeared to be able to "absorb" the uncured epoxy resin during prepreg preparation, which helps to form a transient interphase between silk and epoxy resin and strong interface adhesion in the composite. During compression of SCLs, Euler buckling (EB)/fracture crushing (FC) are the two energy absorbing mechanisms in the lattice structures. SCLs exhibited enduring EB and FC mechanisms, leading to up to ~40% compressive strain. The specific energy absorption reached 7 J g^{-1}; considering the specific compressive strength from the Ashby chart in Fig. 3d, SCLs appeared to be superior to other natural FRPs due to the high toughness of the silk composites. We believe that these lightweight structure designs serve to further improve the service efficiency of silk-based composites for energy absorption applications.

5. Conclusions and prospects

In this brief article, we have reviewed our recent studies on natural silkworm silks and corresponding composites that utilize continuous silk fibres/woven fabrics as reinforcements. Given the understanding on the structure characteristics of natural silkworm silks from *B. mori* and *A. pernyi* silkworms, we designed and fabricated pure silk reinforced composites including *Bm*-SFRPs and *Ap*-SFRPs, hybrid fibre reinforced composites including *Bm*-flax HFRPs and *Ap*-carbon fibre HFRPs, and lightweight lattice structures. These composites exhibit a wide spectrum of mechanical properties, *i.e.,* 100–400 MPa for tensile strength and 50–120 kJ m^{-2} for unnotched Charpy impact strength. Hybridization with stronger fibres and design for lattice structures are effective approaches to accelerate the engineering application of silk-based composites. We believe that the continuous exploration of multi-scale toughening mechanisms in natural silks and their composites can contribute to the development of new biomimetic materials. In the future, systematic studies on estimating the silk-matrix polymer interface properties, predicting the mechanical behavior of SFRPs and looking for novel matrix polymers (i.e., fully absorbable and biocompatible biopolymers) are an imperative theme for the application of SFRPs beyond the laboratory.

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.

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