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Comparison of toughening mechanisms in natural silk-reinforced composites with three epoxy resin matrices

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ABSTRACT

Natural silk fibre can reinforce the polymer matrix for composites with improved toughness and impact strength. However, the optimum selection of matrices for the mechanical performance of silk fibre reinforced plastics (SFRPs) is still unclear, especially with respect to toughness. Here Bombyx mori silk is applied to reinforce three epoxy resin matrices with various crosslinking structures. The epoxy resin from bisphenol-A epoxy and aliphatic diamine precursors that is the most ductile and the toughest leads to the SFRPs with the highest tensile breaking energy (14.1 MJ·m⁻³) and impact strength (110 kJ·m⁻²). Examination of the toughening mechanisms in these composites, which haveeither a brittle or ductile matrix, indicated the predominance of crack propagation and fibre pull-out to increase specific energy dissipation during the fracture processes. The rationale for this study is to provide guidelines for the design of matrices in SFRPs with optimal toughness, by identifying the salient toughening mechanisms in these tough and ductile fibre-reinforced composites.

1. Introduction

Natural fibres have emerged as a "green" reinforcement in fibrereinforced polymers (FRPs) for secondary load-carrying structural materials in engineering applications [1,2]. Advantages, such as low density, good mechanical properties and biodegradability, make plant fibre attractive to researchers and the industry [3,4]. Being another natural fibre, silk fibre produced by animals, especially silkworms, possesses even lower density (1300 kg·m⁻³) than plant fibers and balanced strength and toughness. Another advantage of natural silk is its stretched length of more than 1000 m for a \sim 20 μ m thin filament, which can be knitted and woven into neat and compact fabrics for garment or composite uses. This makes it the "textile queen" prior to the emergence of synthetic fibres. Recently, silk fibre/fabric reinforced plastics (SFRPs) with high silk volume fractions, *i.e.*, $V_{\rm f} \sim 70\%$, have shown much improved toughness compared to that of the unreinforced matrix and plant fibre reinforced plastics (PFRPs) [5-9]. A further advantage of SFRPs is their high specific impact strength measured in Charpy impact testing, which can approach values obtained for glass fibre reinforced plastics (GFRPs). Additionally, SFRPs show sound interfacial strengths of 30–40 MPa measured in interlaminar shear strength tests [6,8]. In China, the cocoon production from Bombyx mori silkworms has been over half a million tons every year for the past decade. In light of this, the tough and ductile natural silk fibre could offer an alternative/supplement reinforcement for FRPs designed for impact-critical engineering applications.

In order to optimize the mechanical performance of SFRPs, research in this field has primarily focused on the following aspects: (i) exploring the best fabrication methods, including hot-press molding [8,9], vacuum-assisted resin transfer molding [10] and winding processes [7,11]), (ii) studying the effect of silk volume fraction [8], (iii) varying silk formats including woven and unwoven fabrics, unidirectional prepreg and short fibres [6,12,13], (iv) hybridizing with other high stiffness and high strength fibres including carbon fibres [10,14–16], and (v)

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modifying the interface properties between the silk and polymer matrix [12,17,18]. Silk fibres generally exhibit improved toughness with an order of magnitude larger breaking strains, of ~20% for *Bombyx mori* [9,19] and ~40% for *Antherea pernyi* [9,20] fibers, as compared to carbon fibres and aramid fibres. These studies have helped to accelerate the development of high toughness SFRPs, but certain challenges remain, such as improving the compatibility between the silk and the matrix and understanding the nature of the failure mechanisms.

Matrix polymers for FRPs are generally categorized into thermoplastics and thermosets, which plays a vital role in determining the mechanical properties of FRPs [21]. For thermoplastics, $poly(\epsilon$ -caprolactone) [22,23], poly(butylene succinate) [13] and poly(lactic acid)[24] have been adopted as bioabsorbable and biodegradable matrices, which are usually suitable for biomedical engineering. On the other hand, SFRPs with a thermosetting matrix have been mostly utilized as structural materials. Epoxy resin has been a popular matrix owing to its high stiffness and strength from the dense chemical crosslinking structure, but this often leads to brittleness and low extensibility; resolving such issues requires the addition of further toughening agents such as rubber fillers [25], thermoplastic fillers [26], and nanoparticles [27]. Previously studied matrix polymers for silk reinforcement include EPI-KOTETM Resin RIMR135 with curing agent RIMH137 [6], epoxy resin AA0341A with curing agent AA0341B [7], epoxy resin E51 with curing agent DS-300G [8], and unsaturated polyester resin 150HRBQNTNW with curing agent MEKPO [15,28]. For certain epoxy resin brands, the detailed molecular structures and composition of the epoxy and



Fig. 1. Chemical structures of (a) the epoxy E51, (b) the epoxy system 1564 including a bisphenol epoxy and an aliphatic epoxy, (c) the curing agent system 3486, and (d) the curing agent D400. (e) Proposed curing reactions between epoxy groups and amino groups. *(Regretfully, the chemical structure of the curing agent DS-300G is a commercial secret and thus could not be acquired.) The three cured epoxy resin matrices are termed EP1 for E51 + DS-300G, EP2 for 1564 + 3486 and EP3 for E51 + D400. (The "n" in the molecular formula in (a) is in the range 0-10.) (f) Schematic illustrations of the three epoxy resin systems. Note that the functional groups in the curing agents are represented here by the amine group only. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

hardeners are not publicly available and so investigating the curing kinetics can be challenging. Therefore, our approach here is to compare commercially available epoxy resins with various crosslinking chemistries in order to seek a sound understanding of the compatibility between silk and epoxy resin species.

To date, little research has focused on the effect of the matrix type with regard to the chemical structure and mechanical characteristics on the mechanical performance of SFRPs. Our aim is to establish the relationships between the structure of the epoxy resin matrix and the toughness for natural silk fibre composites. These findings are intended to provide guidelines for the rational design of superior SFRPs and to offer insights into the impressive toughness properties of these ductile fibre-reinforced composites.

2. Materials and methods

2.1. Materials

Three matrix epoxy resins were selected: (i) E-51 and curing agent DS-300G with a mass ratio of 100:84, supplied by Dasen Material Science &Technology. Inc. (Tianjin, China), (ii) Araldite LY1564 and curing agent Aradur3486 with a mass ratio of 100:34, produced by the Huntsman Company (Utah, USA), and (iii) E-51 and curing agent polyamide D400 with a mass ratio of 100:58, supplied by Huazheng Composites Co., Ltd.(Shanghai, China). Their chemical structures and the schemes for the curing reaction of the epoxy resin precursors are shown in Fig. 1. The three cured epoxy resin matrices are termed EP1 for E51 + DS-300G, EP2 for 1564 + 3486 and EP3 for E51 + D400.

A plain woven *Bombyx mori* silk fabric (areal density of 90 ± 5 g. m⁻²), purchased from Huzhou Yongrui Textile Co. Ltd. (Zhejiang, China), was utilized as the reinforcement. The density of this reinforcement was taken to be 1.3 g.cm⁻³ [29]. The crystalline structure of *Bombyx mori* silk was characterized by FTIR and wide-angle X-ray scattering; details of the methods and results are shown in Fig. S1. The degree of crystallinity was calculated at 34% in our previous work [16]. Specifically, the crystalline regions in silk mainly contribute to its high stiffness and strength whereas the amorphous regions contribute to its high toughness [16].

2.2. Fabrication of composites

SFRPs laminates with a size of 200 mm \times 100 mm were fabricated using traditional lay-up procedures followed by hot-press molding (Hotpress Machine, Qingdao Huabo Machinery Technology Co., Ltd). In the hot-press process, we used a ~300 kPa pressure for all laminates, with the curing parameters set as: (i) EP1: 2 hr at 120 °C, (ii) EP2: 8 hr at 80 °C, and (iii) EP3: 3 hr at 100 °C. Two volume fractions, of $V_{\rm f} = 30\%$ and 60%, were chosen to study the influence of fibre content and interactions with the various epoxy resins. In this work, SFRPs are termed SFRP-30% and SFRP-60%, respectively. Silk volumes were calculated for the target fibre volume fractions in the composite; these were added during the lay-up. The total volume of the composites was controlled by a stainless steel frame with set sizes. In addition, we changed the curing agent content for EP2 with different mass ratios of (1564:3486): 100:29, 100:34 and 100:39. Corresponding EP samples were defined as EP2-29%, EP2-34% and EP2-39%, respectively. The composites were defined as SFRP-EP2-29%, SFRP-EP2-34%, SFRP-EP2-39%, respectively. The silk volume fraction of the SFRPs was set as 60%.

2.3. Processing performance of epoxy resin

Dynamic shear rheology measurements were performed with a Rheometer (DHR-2, TA, USA) using a parallel plate (diameter $\Phi = 25$ mm) under oscillation mode to acquire the time-temperature-viscosity behaviour. The frequency and strain were set at 1 Hz and 1.4%, respectively. Heating and holds at temperatures were programmed

according to the curing parameters of the different epoxy resins; these parameters can be found in Fig. S3 in the Supplementary Information.

2.4. Quasi-static mechanical tests for SFRPs

Uniaxial tensile properties were conducted according to the Chinese Standard GB/T1040-92 test procedure using an Instron 8801 screwdriven universal testing machine (Instron Corp., Norwood, MA, USA). Flexural properties were obtained in accordance with Chinese Standard GB/T1449-2005 using an Instron 5565 screw-driven testing machine. The displacement rate for both tensile and flexural tests was set at 2 mm·min⁻¹.

2.5. Interlaminar shear strength testing

Interlaminar shear properties were also measured on an Instron 5565 testing machine. The displacement rate for these tests was set as 1 mm \cdot min⁻¹, in accordance with International Standard ISO 14130:1997.

2.6. Impact testing

Charpy impact testing was carried out according to International Standard ISO 179:1997 on an MTS model ZBC 1000 Charpy pendulum testing machine (MTS Corp., Eden Prairie, MN, USA) utilizing a 4 J hammer.

2.7. Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis (DMTA) was conducted on a dynamic mechanical analyser (TA Instruments, Waters Ltd., DMA Q800) under three-point bending mode at a constant frequency of 1 Hz. The strain and heating rate were respectively set at 0.2% and 3 °C min⁻¹.

2.8. Differential scanning calorimetry (DSC) analysis

The DSC measurements were carried out with a Mettler Toledo Instruments DSC1 (Zurich, Switzerland). The tests were performed with a nitrogen flow of 10 mL min⁻¹. The heating rate was set as 3 °C min⁻¹ over a temperature range of 25–300 °C.

2.9. Microstructural analysis of fracture surface

Fracture surfaces were observed by scanning electron microscopy (SEM, JEOL JSM-6010, Japan) using the secondary electron mode with a 20 kV accelerating voltage.

2.10. Micro-droplets test

The micro-droplets of uncured epoxy resin were carefully placed on individual silk fibres. The size of micro-droplets was controlled to less than 100 μ m to ensure that the silk fibre would not fracture during the test. The test was conducted on a fiber/resin composite interface performance tester MODEL HM410 (Toyo Industries Co., Ltd, Japan). The loading rate was set at 0.1 mm min⁻¹. At least 20 samples were tested for each EP matrix.

2.11. Cohesive finite element simulation

To simulate the interface damage and fracture process in the composite, cohesive finite element modeling was used based on a linear constitutive traction separation law determined by a damage initiation criterion, a damage evolution criterion and a softening law. Cohesive elements were adopted to simulate the interface of the fibre and the matrix. The initiation of cohesive damage was defined by the Quads Damage criterion, which is expressed as:

$$\left\{\frac{\langle t_n \rangle}{t_n^0}\right\}^2 + \left\{\frac{t_s}{t_s^0}\right\}^2 + \left\{\frac{t_t}{t_t^0}\right\}^2 = 1$$
(1)

where t_i^0 (*i* = *s*, *t*, *n*) is respectively the cohesive shear, tensile and normal strengths at damage initiation. If the symbol < > returns only positive values, it implies the compression load does not initiate damage. The stiffness degradation is controlled by the separation, which can be described by the damage variable *D*:

$$D = \frac{\delta_m^f (\delta_m^{max} - \delta_m^0)}{\delta_m^{max} (\delta_m^f - \delta_m^0)} \tag{2}$$

where $\delta_m = \sqrt{\langle \delta_n \rangle^2 + \delta_s^2 + \delta_t^2}$, δ_m^0 and δ_m^f represent the separation at damage initiation and complete failure separately, and δ_m^{max} is the maximum value of the resultant displacement. When *D* reaches 0.999, the element is deleted.

A unit cell model of the SFRPs containing 9 silk fibres with the fibre volume fraction of 60% was employed. The size of the model was $54 \times 54 \times 27 \ \mu m^3$ with a fibre diameter of 7.9 μ m. The cohesive elements were inserted into the interface of the fibre and matrix to simulate the interfacial bonding of the composite. The bottom of the model was fixed with a tensile displacement applied to the top. The mechanical properties of the fibre and matrix used in the simulation, specifically the stiffness, strength and toughness, were obtained from the tensile experiments and considered to be isotropic. The mechanical parameters of the fibre and the matrix used in the simulations are shown in Table S1. The plastic behaviour is fitted from the tensile data in the experiment. Ductile damage criteria were applied for the failure of both the fibre and matrix. The cohesive parameters of the interface are shown in Table S2. The finite element simulations were conducted using the commercial ABAQUS software.

3. Results

3.1. Quasi-static mechanical properties of SFRPs

The detailed chemical structures of the epoxy precursors and curing agents as well as the various crosslinking structures are illustrated in Fig. 1. EP1 comprises a crosslinked structure with more rigid segments from the epoxy precursor and the curing agent, giving it a high stiffness. The epoxy precursor and the curing agent in EP2 contains both rigid and flexible segments, which result in a balanced stiffness and enhanced ductility in its crosslinked structure. In comparison, EP3 combines a rigid epoxy precursor and a linear flexible curing agent; this crosslinked structure turns out to be the least stiff and very ductile.

Tensile mechanical properties of these epoxy resins were compared using the uniaxial tensile stress-strain curves shown in Fig. 2a. The EP1 and EP2 epoxy resins showed similar tensile moduli (respectively, 3.2 GPa and 2.9 GPa) and tensile strengths (76.6 MPa and 72.3 MPa), but the EP2 epoxy resin with its flexible chain structure displayed a higher elongation (7.1%). The third epoxy resin EP3 with the flexible curing agent polypropylene glycol bis(2-aminopropyl ether) exhibited the lowest modulus (1.8 GPa) and strength (32.7 MPa) but a much higher elongation (62%).

The tensile behavior of SFRPs manufactured from the three epoxy resins with two fibre volume fractions ($V_f = 30$ and 60 vol%) are compared in Fig. 2b-d. The breaking energy was calculated from the area under tensile curves to provide an evaluation of the toughness. In all cases, the composites exhibited an enhanced modulus and strength as compared to the pristine epoxy resins.

The fibre/matrix modulus ratio (E_f/E_m) is an important consideration in the design of composites [24]. To increase the load carried by the fibres relative to the matrix, *i.e.*, the P_f/P_m ratio in the initial elastic deformation stage, a simple approach is to increase the E_f/E_m ratio.



Fig. 2. Tensile properties of the three epoxy resins and SFRPs. (a) Uniaxial tensile (engineering) stress-strain curves of the epoxy resins and 30 vol% and 60 vol% SFRPs, and their (b) tensile modulus, (c) tensile strength, and (d) breaking energy. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 3. Ratio of the loads carried by the fibre and the matrix, P_f/P_m , as function of the ratio of the modulus of the fibre and the matrix, E_f/E_m , where V_f is the fibre volume fraction. Note: this prediction model is applicable for the linear elastic deformation region prior to yielding. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 3 shows the SFRPs with $V_f = 60$ vol% with the EP1 and EP2 matrices where a low E_f/E_m ratio (~2) can be seen to lead to low P_f/P_m (~3). However, for the SFRPs with the EP3 matrix, a higher $E_{\rm f}/E_{\rm m}$ ratio resulted in $P_{\rm f}/P_{\rm m}$ ratios exceeding 5, which would be expected to better utilize the toughness properties of the silk reinforcement. As shown in Fig. 2c, the SFRP-60 vol% composite, with the lowest stiffness EP3 matrix, exhibited the highest tensile strength (176.3 MPa) and the largest overall breaking energy (14.1 MJ.m⁻³). In fact, the breaking energy for the 30 vol% was lower than for the pure EP3. This could be attributed to the brittle failure mode in the SFRP-EP3 composite with 30 vol% silk, which significantly reduced the breaking strain and breaking energy. However, when the silk content was increased to 60 vol%, the stiffness and strength of the composite were elevated markedly with similar breaking strains as the 30 vol% SFRP-EP3, leading to an improved breaking energy. Nevertheless, it is clear that the use of a ductile epoxy resin matrix with too low a modulus can lead to significantly reduced flexural strength of the composite (Fig. S2). It is important to note that the 60 vol% SFRP-EP3 composite deformed and did not fail with similar damage modes, *i.e.*, interfacial delamination, to that in the EP1 and EP2 composites at flexural strains exceeding 10%. Clearly, the 60 vol% SFRP-EP3 failed by tensile yielding. As the tensile yield stress of 60 vol% SFRP-EP3 was much smaller than for the other two composites, the flexural strength was the lowest for the EP3 system.

The interlaminar shear strengths (ILSS) of the SFRPs are shown in Table 1. SFRPs with an EP3 resin matrix exhibited the highest ILSS (43.2 MPa). Compared with PFRPs, the ILSS values for all the SFRPs were ~ 2

Table 1

Interfacial shear strength(IFSS) from micro-droplet tests and interlaminar sh	ieai
strength (ILSS) of SFRPs with different epoxy resin matrices ($V_{\rm f} = 60\%$).	

Epoxy resin matrix	IFSS (MPa)	ILSS (MPa)
SFRP-EP1	$\textbf{6.4} \pm \textbf{2.7}$	$\textbf{32.9} \pm \textbf{2.3}$
SFRP-EP2	21.6 ± 4.4	35.3 ± 1.5
SFRP-EP3	$>41.2\pm3.2$	43.2 ± 1.9

Note: The accurate value of IFSS for SFRP-EP3 could not be measured because the maximum shear force exceeded the maximum tensile force of a single silk fibre.

to 3 times larger with similar epoxy resin matrices [30,31]. Furthermore, the interfacial shear strengths (IFSS) were obtained from microdroplet tests; results are listed in Table 1. Silk-EP3 composites showed the highest IFSS values (greater than 41.2 MPa), which was at least two times larger than that of the Silk-EP2 (21.6 MPa). The Silk-EP1 exhibited the lowest IFSS value of 6.4 MPa. Both interlaminar and interfacial shear strengths exhibited a similar tendency of EP3 > EP2 > EP1. Based on the evidence presented here, we propose that the combination of aromatic epoxy precursors and aliphatic amine curing agents is likely to be more chemically compatible with the silk fibres, leading to the best interfacial adhesion. However, the detailed mechanisms underlying this behaviour require further study. It is also worth noting that the deformation behaviour of the silk and epoxy resin composites for the EP3 system is different from that for EP1 and EP2 systems. During the measurements of IFSS and ILSS, the EP3 composite systems always exhibited the lowest stiffness but the highest ductility.

To further understand the molecular interactions of the silk and epoxy resin, we investigated the compositional variations of the epoxy precursors and curing agents for EP2, and compared the interfacial bonding strengths and tensile properties of SFRPs. Two additional mass ratios of 29% and 39% were examined, representing compositions deficient in curing agents and with excessive curing agents, as compared to the commercially recommended ratio of 34%. Silks contain tyrosine and lysine residues with active hydrogen species, which can react with epoxy groups to form covalent interactions; the serine residues with the hydroxyl groups increase the non-covalent interactions such as hydrogen bonding with the epoxy resins [18]. The largest exothermal peak in the DSC curves of Fig. 4a indicated that the 34% ratio was the perfect stoichiometry of epoxy and active hydrogen containing species, leading to the largest degree of crosslinking (Table S3). The other two ratios led to less crosslinked EP matrices. The DMA results in Fig. 4b show the glass transition temperature $T_{\rm g}$ for EP2-29% to be the lowest at 87 °C.

Further experimental interfacial shear measurements gave the interfacial strengths for the various silk-EP2 composites shown in Fig. 4c; these results followed a similar trend to that from DSC and DMA measurements, namely the interfacial strengths for SFRP-EP2-34% > SFRP-EP2-39% > SFRP-EP2-29%. This suggests that the interfacial shear strength is largely determined by the degree of crosslinking of the EP matrix for the same epoxy resin precursors. An optimized ratio of epoxy precursor and curing agent may exist in a narrow range around the stoichiometric ratio to improve silk-EP interfacial strength; however, this requires significant further study.

3.2. Impact properties

Impact strength is a critical property for SFRPs as their anticipated applications invariably involve shock resistance, such as for bullet-proof helmets and surfboards [6]. As mentioned above, compared to PFRPs, SFRPs have the advantage of a higher impact strength [9,16]. Indeed, in the present study, the impact strengths for all the SFRPs, measured in unnotched Charpy impact tests, exceeded the corresponding values for PFRPs (which are usually below 10 kJ.m⁻² [6]), as shown in Fig. 5. The SFRP-60 vol% with EP3 resin matrix displayed the highest impact strength (110 kJ.m⁻²), which was, respectively, 55% and 34% larger than that of the SFRP-60 vol% with an EP1 and EP2 resin matrix. It is clear that combining a ductile epoxy resin matrix with silk reinforcements can markedly promote the impact strength of the composite. Notably, the ductile EP3 resin also showed much larger ILSS and IFSS values, suggesting that sound interface properties can enhance the impact strength by controlling potentially deleterious fracture mechanisms such as delamination.

3.3. Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical thermal analysis (DMTA) was performed to



Fig. 4. Comprehensive properties of the EP2s matrices and their composites SFRPs with different mass ratios for curing agents of 29%, 34% and 39%. 34% is the recommended mass ratio by the supplier. (a) DSC thermogram results for the EP2s during curing. (b) Loss factor tan δ for cured EP2s from DMTA tests (the glass transition temperature T_g of each sample is marked in the figure). (c) Interfacial shear strengths between silk and various EP2s using micro-droplet tests. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 5. Impact strengths of the SFRPs with three epoxy resins and two fibre volume fractions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

evaluate the storage modulus (E') and the damping properties of the SFRPs as a function of temperature. DMTA is more sensitive to detecting the glass transition in polymers than other thermal analysis techniques such as differential scanning calorimetry. For fibre reinforced composites, the glass transition of the matrix polymer is affected by the type and volume fraction of the reinforcement fibre and the interfacial fibre-

matrix properties. The glass-transition temperature (T_g) identified by the peak temperature of the loss tangent tan δ peak and its shift is often used to indicate the nature of the fibre-matrix bonding [32].

The storage modulus E' and tan δ of the SFRPs over the range 25 °C to 175 °C are presented in Fig. 6a, c. The E' values at 25 °C and 150 °C, i.e., below and above Tg, are summarized in Fig. 6b. An increase in silk fraction from 30 to 60 vol% increased the E' of the SFRPs at 25 °C although the value E' remained above 1 GPa at 150 °C. The measured T_g of the 60 vol% silk composites was 115 °C with the EP1 matrix; with the EP2 matrix, it was reduced to 100 °C and further reduced to 50 °C with the EP3 matrix. It might be anticipated that the introduction of silk fibres in SFRPs would elevate the T_g compared to that of the pure epoxy resin matrix, as has been observed in CFRPs [16], as the T_g of silk, which is typically \sim 220 °C, is much higher than that of the epoxy resins [33]. Nevertheless, results in Fig. 6c indicate the contrary, that the T_g values of all the SFRPs were lower than that of the unreinforced matrix. For example, for the SFRP-60 vol% with EP1, the $T_{\rm g}$ was 15 °C lower than that of the pristine EP1 matrix. It is believed that this is due to the epoxy resin at the matrix/silk interfaces being less crosslinked, i.e., more mobile, compared to that in the bulk epoxy resin where a high degree of crosslinking is far more prevalent. This is because the CFRPs sizing agents are usually applied on the surface of commercial carbon fibres, which can result in an interfacial phase with a higher degree of crosslinking than the bulk matrix, and to an increase in the T_g of the composite. However, for the silk-epoxy resin interface, the silk fibres are untreated and covalent/crosslinking interactions are not prevalent. In addition, Fig. 6d shows the calculated area under curves of tan δ from



Fig. 6. Dynamic mechanical property profiles of the different epoxy resins and SFRPs, measured in three-point bending: (a) storage modulus E', and (c) loss factor tan δ , both as a function of temperature from 25 °C to 170 °C, (b) Comparison of the E' values of various SFRPs at 25 °C to 170 °C, (d) Area under the curve from (c) tan δ as a function of temperature. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 6c. With increasing silk fibre content, all the SFRPs with varied EP matrices exhibited a similar trend of a decrease in the accumulated tan δ , indicating the decreasing number of epoxy resin segments and their motions. With 60 vol% silk composites, all the SFRPs exhibited very similar values of the accumulated tan δ (~13), indicating that the segmental motions of the epoxy resin matrices during the glass transition reached a low plateau, corresponding to the high storage moduli of the SFRPs (exceeding 5 GPa).

3.4. Processing performance of epoxy resin

The rheological behaviour of epoxy resin is often optimized for the processing of thermosets [34]. Fig. S3 shows the time-temperatureviscosity curves of three epoxy resin systems heated at 3 °C min⁻¹ to above T_{α} prior to an isothermal hold. The viscosity of the three systems initially decreased to a low (platform) level, then sharply increased rising to a plateau region. The key processing properties, including the viscosity at room temperature (RT), the activation energy for viscous flow (E_n) in the initial descending and lower platform regions, and the time during the subsequent ascending region, are shown in Table 2. The viscosity values at room temperature were 0.58, 0.22 and 1.72 Pa.s for the EP1, EP2 and EP3 resins, respectively. The activation energy E_n was calculated using the Arrhenius equation following the procedure given in the Supplementary Information [35,36]. From Fig. S4, the E_n activation energy of the EP2 epoxy was 17.4 kJ.mol⁻¹, *i.e.*, one order of magnitude lower than that for EP1 and EP3. A lower activation energy has been reported to result in lower temperature fluctuations and better processing control [35]. Moreover, the EP2 and EP3 matrices exhibit a broader ascending region and longer gelation time than EP1, which allows liquid resin to infiltrate within a wider pressurized time window and avoid incomplete impregnation. Taken together, the EP2 matrix can

Table 2

Comparison of the mechanical properties the SFRPs based on the three epoxy resins.

Performance		EP1	EP2	EP3
Tensile performance	Young's modulus (GPa)	3.2	2.9	1.8
	Tensile strength (MPa)	76.6	72.3	32.7
	Tensile elongations (%)	2.8	7.1	62.0
	Tensile breaking energy (M.I.m ⁻³)	1.1	4.0	14.2
Flexural performance	Flexural strength (MPa)	134.2	163.1	66.0
Impact performance	Impact strength (kJ. m ⁻²)	12.8	18.3	60.0
Thermal mechanical performance	Glass-transition temperature (°C)	115	100	50
	tan δ at RT (25 °C)	~0.03	~0.03	~ 0.06
Processing	viscosity at RT (Pa.S)	0.58	0.22	1.72
performance	E_{η} in descending region (kJ.mol ⁻¹)	600.6	553.0	340.9
	E_{η} in platform region (kJ.mol ⁻¹)	257.7	17.4	294.7
	Time range of ascending region (s)	~290	~2170	~2000

Note: E_{η} : activation energy for viscous flow.

be considered to display the best processing performance.

In addition, the curing degree for the three epoxy resins was characterized with DSC (Fig. S5). By comparing the heat of uncured and cured epoxy resin from our procedures, the curing degree for EP1, EP2 and EP3 was calculated to be almost 100%, confirming that the processing conditions that were used were correctly chosen to maximize crosslinking reactions.

4. Discussion

4.1. Comprehensive performance of epoxy resins and SFRPs

The measured properties of the epoxy resins are summarized in Table 2, with a comparative radar plot for SFRPs shown in Fig. 7. For SFRPs, five property indexes, the glass-transition temperature T_{g} , the tensile strength σ_t , breaking energy BE_t , flexural strength σ_f and the impact strength σ_I , are compared. It is apparent that SFRPs with the EP3 matrix exhibited the highest breaking energy and impact strength (toughness properties), the largest tensile strength, yet the lowest flexural strength and T_g ; the use of EP3 with a low T_g could confer a higher ductility and energy dissipation through the motions of rubbery segments. In Fig. 6c, the larger tan δ of ~0.06 for the EP3 matrix at room temperature, compared with that of the EP1 and EP2 matrices, implies that more molecular motions that convert mechanical energy to heat are activated. However, for certain applications a high T_g may be a more important requirement for composites. Therefore, the clear trade-off between high ductility/impact performance and thermal stability for SFRPs should be considered. Accordingly, we would conclude that the EP2 matrix could be a good choice for SFRPs that require a balance of mechanical and thermal-mechanical properties.

4.2. Fracture analysis and toughening mechanisms in SFRPs

Based on the ductility of the epoxy resin matrix, the SFRPs can be divided into brittle and ductile matrix systems, each of which display distinct fracture behaviour. Considering the different interfacial strengths, SFRPs can be further categorized as systems with a brittle matrix + weak interface (EP1), brittle matrix + strong interface (EP2) and ductile matrix + strong interface (EP3). A brittle/ductile matrix would define whether the matrix fracture occurs first; a weak/strong interface would define whether interface failure (*i.e.* debonding) occurs prior to the fibre fracture. Representative fracture morphologies are shown in Fig. 8.

For a brittle matrix system where the fibre fracture strain exceeds that of the matrix ($\varepsilon_{\rm f} > \varepsilon_{\rm m}$), as is the case for the EP2 matrix, the fracture morphology in the SFRPs, shown in Fig. 8a-c, can be seen to display rough ridges around the silk fibres, suggesting a role of the silk in deflecting the crack path. The deflected load then partially acts as the



Fig. 7. Comparative radar plot of the mechanical and thermal properties of the SFRPs in this study. Properties shown are the glass-transition temperature $T_{\rm g}$ (°C), tensile strength $\sigma_{\rm t}$ (MPa), breaking energy $BE_{\rm t}$ (MJ.m⁻³), flexural strength $\sigma_{\rm f}$ (MPa), and impact strength $\sigma_{\rm i}$ (kJ.m⁻²). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

shear force exerted on the fibre/matrix interface, which promotes fibre pull-out. Thus, the primary fracture modes in brittle matrix systems involve matrix fracture, fibre pull-out and fibre fracture. A similar fracture morphology has also been observed for the SFRP with an EP1 epoxy resin matrix [8].

In contrast, flat fracture morphologies are characteristic of ductile matrix systems (Fig. 8d-f), where the matrix fracture strain exceeds that for the fiber ($\varepsilon_{\rm f} < \varepsilon_{\rm m}$), as with the EP3 matrix. In this scenario, due to the lower modulus of the ductile matrix, the fibre sustains a higher load ratio, with both fibre and matrix deforming plastically until failure; this results in a much flatter morphology with fracture initiating in the fibre or interface. Extrinsic toughening mechanisms such as interface debonding and fibre pull-out are also at play in the ductile matrix systems, where the ultimate mechanical properties are dictated by the intrinsic strength and toughness of individual constituents.

Fig. 9 shows some detailed fracture features for the brittle matrix system (SFRPs with EP2). Rough ridges can be seen surrounding the silk fibres normal to their axis, although the fibre-matrix interface appears to be intact, indicating that the cracks mainly initiated within the matrix prior to being arrested at the interface or at the fibre. Given the high IFSS of ~20 MPa for silk-EP2, interface debonding and subsequent fibre pullout was clearly suppressed prior to the final failure in these systems [37,38]. It is interesting to note that the microcracks are generated at the silk-matrix interface due to the deflection of the major cracks and redistribution of stress by the fibre, similar to the fracture morphologies of pure epoxy resins [39,40]; as a mechanism of inelastic deformation, such microcracking and local yielding can provide a contribution to the toughness in SFRPs. In addition, the noted ridges on the fracture plane of EP2 are randomly orientated, suggestive of crack deflection in multiple directions (Fig. 9c); such cracks propagating in different directions can interact and converge, as displayed in Fig. 9d [37], which also will contribute to the toughness.

To further understand the fracture processes, we performed finite element simulations as described in section 2.11; results are shown in Fig. 10, including schematic illustrations of the various fracture modes during deformation to failure of the composites. For the brittle matrices (Fig. 10a) and ductile matrices (Fig. 10b), two levels of interfacial strength were applied to generate a combination of four categories of SFRP composites, covering the above three matrices that we tested experimentally and an additional category of ductile matrix + weak interface. The model with 9 fibres provided a simulation of the stress transfer behaviour among the matrix and fibres, with the "interphase" used to reflect the interfacial properties. Of note is that the interfacial strength (IFS) in the model was set to higher values (i.e., 60 MPa for the brittle matrix + strong interface system in Table S2) than the experimental IFSS in order to simulate interfacial failure after the matrix failure. The von Mises stress values of the silk fibres during the simulated tensile tests are summarized in Table 3, where the average stress and maximum stress values are compared at the point of matrix failure, interfacial failure and fibre failure for the four categories of SFRPs. From these data, it is evident that the ductile matrix systems better utilize the strength potential of the silk fibres than the brittle matrices; indeed, in the ductile matrix systems the average stress of silk fibres at the moment of failure exceeded 390 MPa. Importantly, high interfacial strength in the same matrix system facilitates stress transfer among the constituents, which leads to a higher average stress in the silk fibres and a welldistributed stress-state.

In summary, the numerical model enables the visualization of typical failure modes in SFRPs, and confirms that the selection of epoxy resin matrices can lead to a wide spectrum of mechanical properties, in particular the enhanced toughness of silk fibre reinforced composites.

5. Summary and conclusions

In this study, three typical epoxy resin matrices were selected to modulate the mechanical properties, specifically the stiffness, strength



Fig. 8. SEM images of the fracture morphology of (a, b, c,) SFRPs with an EP2 matrix; (d, e, f) SFRPs with an EP3 matrix. The fracture morphology of SFRPs with an EP1 matrix was evaluated in our previous study [11]; the fracture surface is rougher with more fibre and fibre bundle pull-out compared with that with the EP2 matrix.



Fig. 9. SEM images and schematic illustration of the tensile fracture morphology of SFRPs with an EP2 matrix, showing (a) fibre pull-out, (b) microcrack and crack convergence, (c) crack scattering, and (d) schematic illustration of crack initiation, propagation and scattering. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 10. Schematic illustrations of the salient damage and toughening mechanisms associated with the fracture of the SFRPs based on (a) a tough fibre-brittle matrix system and (b) a tough fibre-tough matrix system. For greater clarity, enlarged images of the simulation results are shown in Fig. S9 in the Supplementary Information. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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Table 3

Maximum and average von Mises stress values of the silk fibres in the finite element model of SFRPs during tensile testing .

Composite category	σ_1 -max	σ_1 -avg	σ_2 -max	σ_2 -avg
SFRP-EP1 (IFS $= 6.4$ MPa)	134.3	120.9	150.7	121.7
SFRP-EP2 (IFS = 21.6 MPa)	186.2	165.3	230.1	204.8
SFRP-EP2 (IFS $= 60$ MPa)	199.7	169.5	277.2	194.3
SFRP-EP3 (IFS = 41.2 MPa)	278.2	245.9	527.9	389.8
SFRP-EP3 (IFS $= 160$ MPa)	527.9	409.8	529.6	401.7

Note: The subscripts 1 and 2 correspond to varied failure modes for each category, referred to Fig. 10.

 $\sigma_1\text{-max:}$ maximum von Mises stress when failure initiates (MPa)

 σ_1 -avg: average von Mises stress when failure initiates (MPa)

 σ_2 -max: maximum von Mises stress when failure propagates to another constituent (MPa)

 $\sigma_2\text{-}\mathsf{avg:}$ average von Mises stress when failure propagates to another constituent (MPa)

IFS: Interfacial strength

and toughness, of silk fibre-reinforced plastic composites (SFRPs). SFRPs with a more ductile matrix (*i.e.* the EP3:E51 + D400) exhibited the highest tensile strength (176.3 MPa), tensile breaking energy (14.1 MJ. m⁻³), and the highest impact strength (110 kJ.m⁻²), which we attribute to the high interfacial shear strength of the SFRP-EP3 and the intrinsic toughness of silk and epoxy resin EP3. Although the ductile SFRPs with the EP3 matrix displayed the best toughness properties, their glass transition temperature was low ($T_g \sim 50$ °C), which may limit their use for certain applications. The SFRPs with a brittle but stiff EP1 matrix exhibited the highest flexural strength (331 MPa).

With respect to the fracture of these SFRPs, the toughening mechanisms in the composites with a ductile matrix *i.e.* EP3, were primarily ascribed to the inherent toughness of silk fibre, whereas in the brittle matrix composites (especially SFRPs with high fibre/matrix interface strength) extrinsic toughening mechanisms such as microcracking and crack deflection largely prevailed. However, to fully optimize the toughness properties, we believe that there is still a need for further research on the interfacial strength of silk-epoxy resin composites. Nevertheless, we trust that the present findings can provide useful guidelines for the future design and development of structural composites from tough fibres and thermosetting matrices.

Credit authorship contribution statement

Kang Yang: methodology, investigation, formal analysis and funding acquisation. Zihong Wu: methodology and investigation. Changgeng Zhou: formal analysis, writing - review & editing. Siyu Cai: formal analysis, writing - review & editing. Zhentao Wu: formal analysis, writing - review & editing. Wenhan Tian: formal analysis, writing review & editing. Sujun Wu: formal analysis, investigation and writing review & editing. Robert O. Ritchie: conceptualization, data curation and writing - review & editing. Juan Guan: conceptualization, formal analysis, funding acquisation, supervision and writing - original draft review & editing.

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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Appendix A. Supplementary material

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