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# Can silk become an effective reinforcing fibre? A property comparison with flax and glass reinforced composites

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ABSTRACT

With the growing interest in bio-based composites as alternatives to traditional glass fibre reinforced composites (GFRPs), there has been a persistent rise in the commercial use of plant fibre composites (PFRPs). In contrast, nature's 'wonder-fibre' silk has had no commercial applications, and only limited scientific investigations, as a composite reinforcement. To produce silk fibre composites (SFRPs) with useful properties, three key recommendations from our critical literature review were followed: (i) a high-failure strain, low-processing temperature thermoset matrix was used to (a) maximise the reinforcing effect of low-stiffness, ductile silk, and (b) facilitate impregnation and avoid fibre degradation, (ii) high fibre volume fractions were employed to ensure that fibres carried a larger fraction of the load, and (iii) given the lack of studies investigating fracture energy dissipation mechanisms in SFRPs, interface modification was avoided due to its complex, sometimes detrimental, effects on toughness. In directly addressing the question, 'is there a case for silks as polymer reinforcements?', we evaluated various mechanical properties of nonwoven and plain woven SFRPs against similar flax and glass composites. In all cases, woven composites performed better than nonwoven composites. While SFRPs were weak in terms of stiffness, their flexural and tensile strength was comparable to PFRPs, but much below that of GFRPs. Notably, the low density of SFRPs, like PFRPs, made them comparable to GFRPs in terms of specific flexural properties. Woven SFRPs exhibited much higher fracture strain capacities than both flax and glass composites, making SFRPs suitable for applications where high compliance is required. The Achilles' heels of PFRPs have been their reportedly (i) inadequate interfacial properties, (ii) inferior impact properties, (iii) poor strength performance, and (iv) high moisture sensitivity. We found that SFRPs outperformed their flax counterparts in areas (i)–(iii), and were more comparable to, but not better than, GFRPs. While concerns such as cost and 'sustainability' of silk are acknowledged, potential applications for SFRPs are discussed.

## 1. Introduction

Biocomposites reinforced with plant fibres such as flax, jute and hemp have been widely investigated in literature as potential eco-friendly alternatives to synthetic fibre reinforced composites [1–4]. In general, the low cost, low density and sustainable nature of plant fibres make them attractive in comparison to the commonly used reinforcing fibre, E-glass (Table 1). While the mechanical strength (absolute and specific) of plant fibre reinforced composites (PFRPs) is generally lower than that of glass fibre reinforced composites (GFRPs), PFRPs may be suitable replacements to GFRPs in stiffness-critical applications (Fig. 1) [5,6]. Consequently, a persistent rise in the commercial use of PFRPs, primarily in the automotive industry, has been observed over the past several years [7].

In contrast, silk, the only natural fibre to exist as a continuous filament, has had no commercial applications, and only limited scientific investigations, as a reinforcement for non-biomedical composites. The question arises: is there a case for silks as suitable polymer reinforcements? More specifically, what advantages do silks and their composites offer in comparison to plant fibres and their composites, and glass fibres and their composites?

### 1.1. The case for silk fibres as reinforcing agents

Many arthropod animals, including silkworms, spiders, scorpions, mites and fleas, have evolved to spin task-specific fibrous protein polymers into fibres for a variety of functional uses: from protection (through structural cocoons or sacs) to prey capture

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**Table 1**
Comparison of the economic, technical and ecological properties of silk, plant and glass fibres.

| Properties | Silk fibres[a] | Plant fibres[b] | Glass fibres[c] |
|---|---|---|---|
| *Economy* | | | |
| Annual global production of fibres (tonnes) | 150,000 | 31,000,000 | 4,000,000 |
| Distribution of fibres for FRPs in EU (tonnes) | 0 | 60,000 | 600,000 |
| Cost of commercial raw fibre (£/kg) | 2.0–30.0 | 0.5–1.5 | 1.3–20.0 |
| *Technical* | | | |
| Chemical nature | Proteinaceous | Lignocellulosic | Silica-based |
| Fibre length | continuous | discrete | continuous |
| Fibre diameter (apparent) (μm) | 1–15 (8–15) | 15–600 (15–30) | 5–25 |
| Density (g cm$^{-3}$) | 1.25–1.35 | 1.35–1.55 | 2.40–2.70 |
| Moisture absorption (%) | 5–35 (20–35) | 7–25 (7–10) | 0–1 |
| Softening temperature (°C) | 170–220 | 190–230 | 700–1,100 |
| Tensile stiffness (GPa) | 5–25 (5–15) | 30–80 (50–80) | 70–85 |
| Tensile strength (GPa) | 0.2–1.8 (0.3–0.6) | 0.4–1.5 (0.5–0.9) | 2.0–3.7 |
| Specific tensile stiffness (GPa/g cm$^{-3}$) | 4–20 (4–12) | 20–60 (30–60) | 27–34 |
| Specific tensile strength (GPa/g cm$^{-3}$) | 0.1–1.5 (0.3–0.7) | 0.3–1.1 (0.3–0.7) | 0.7–1.5 |
| Tensile failure strain (%) | 15–60 (15–25) | 2–30 (2–4) | 2.5–5.3 |
| Toughness (MJ m$^{-3}$) | 25–250 (70) | 5–35 (7–14) | 40–50 |
| Specific toughness (MJ m$^{-3}$/g cm$^{-3}$) | 20–185 (50–55) | 3–26 (4–10) | 16–19 |
| Abrasive to machines | No | No | Yes |
| *Ecological* | | | |
| Embodied energy of commercial raw fibre (MJ/kg)[d] | 50–100 | 4–15 | 30–50 |
| Renewable source | Yes | Yes | No |
| Recyclable | Yes | Yes | Partly |
| Biodegradable | Yes | Yes | No |
| Hazardous/toxic (upon inhalation) | No | No | Yes |

[a] Includes silks from various spiders and silkworms. As most of the commercial silk is cultivated from the *Bombyx mori* silkmoth, figures in brackets present the typical properties of this variety of silk. The composites manufactured in this study also employ *B. mori* silk. Data from [44,55,59,62,63] (and references therein).

[b] Includes bast, leaf and seed fibres, but does not include wood and grass/reed fibres. Figures in brackets present the typical properties of flax fibre. Data from [1,64] (and references therein).

[c] Includes E- and S-glass fibres. Properties for E-glass are in the lower range, in comparison to S-glass. Data from [1,64] (and references therein).

[d] The conversion of silk fibres in cocoons into reeled slivers and later aligned textile products can further increase the cumulative energy demand, for instance, to up to 1850 MJ/kg for raw silk slivers [59]. Similarly, while the energy required in the cultivation of plant fibres is low (4–15 MJ/kg), further processing steps (*e.g.* retting and spinning) can significantly increase the cumulative energy demand, for instance, to up to 146 MJ/kg for flax yarn [3,61,65]. Glass fibres, on the other hand, are produced through an extrusion process and can be converted into reinforcements for composites (in the form of chopped strand mats or aligned fabrics, for instance) without significant energy input.

(using webs) [8–11]. It is this large group of fibres that we call silks. Silk from the cocoons of the domesticated mulberry silkworm, *Bombyx mori* is of particular economic importance and is generally used in luxurious textiles.

Importantly, the biocompatibility and bioresorbable properties of silks, their amenability to aqueous or organic solvent processing into various ‘regenerated’ forms (including aqueous solutions, films, hydrogels, porous sponges, regenerated fibres and cords, and nonwoven mats), alongside their unique combination of high strength and toughness, make them ideal for a wide range of clinical applications: from braided suture threads for surgical options, to porous, reinforced-composite scaffolds for cartilage and bone repair [8–11]. Naturally, considerable research has focussed on biocomposites based on regenerated silks for such biomedical applications [8–11].

Nevertheless, many of the properties of native silks (as opposed to regenerated silks) also make them potential sustainable alternative reinforcement materials, alongside plant fibres, for engineering (*i.e.* non-biomedical) composites. This forms the focus of our research. Table 1 compares the economic, technical and ecological properties of silks with plant and glass fibres. In general, the primary disadvantages of silks in comparison to plant and glass fibres are: (i) higher cost, (ii) lower annual production, (iii) higher moisture absorption, (iv) lower softening (and therefore processing) temperatures, (v) poor stiffness, and (vi) high embodied energy for processed materials (*e.g.* fabrics). However, they possess (i) lower density (than even plant fibres), (ii) natural flame resistance (iii) moderate strength, (iv) unparalleled toughness (higher than even Kevlar), and (v) a generally favourable environmental profile of the raw material. Other technical advantages of silks specific to composites applications include (i) their naturally continuous length, and (ii) the high compressibility of silk preforms [12]. While the former would translate to a high fibre length distribution factor $\eta_l$ and therefore reinforcing effect in composites, the latter provides an opportunity to produce high fibre volume fraction natural fibre composites [12].

### *1.2. A critical literature review on silk fibre composites*

From a general perspective, the limited literature available on mulberry silk fibre reinforced polymers (SFRPs) principally attempts the investigation of two types of composites: (i) biodegradable or bio-based composites for non-structural applications, and (ii) tough composites for energy-absorbing and crashworthy structures. Most studies have employed low fibre weight fractions, ranging between 1% and 30%.

In the first case, short silk fibres (0.5–10 mm in length) have been incorporated as reinforcements for (i) thermoplastic polymers (such as biodegradable polylactic acid and polybutylene succinate, and non-biodegradable polypropylene) [13–18], or (ii) elastomeric rubbers (both natural and synthetic) [19,20], via extrusion/injection moulding processes. Notably, the use of screws and mixers in such manufacturing processes leads to (i) the 3D dispersion and spatial ‘random’ orientation of the anisotropic fibres, and (ii) the breakage of chopped short silk fibres (<10 mm in length) into even shorter fibres ($l_f$ = 0.3–2.0 mm in length) [1,19–21]. The former leads to fibre orientation distribution factors $\eta_o$ in the range of 0.20 (nominally-3D fibre dispersion) to 0.37 (some preferred orientation of fibres) [1]. Reinforcing fibre length $l_f$, on the other hand, affects the fibre length distribution factor of discontinuous fibre