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Spider silk reinforced by graphene or carbon nanotubes

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Abstract

Spider silk has promising mechanical properties, since it conjugates high strength (~1.5 GPa) and toughness (~150 J g^{-1}). Here, we report the production of silk incorporating graphene and carbon nanotubes by spider spinning, after feeding spiders with the corresponding aqueous dispersions. We observe an increment of the mechanical properties with respect to pristine silk, up to a fracture strength ~5.4 GPa and a toughness modulus ~1570 J g^{-1}. This approach could be extended to other biological systems and lead to a new class of artificially modified biological, or 'bionic', materials.

Introduction

Silkworm silks have been widely used by mankind for millennia, but only recently their mechanical properties and structure have been investigated in depth [1, 2]. An increasing number of studies also focuses on spider silk, due to its promising mechanical (~10 GPa Young's modulus, ~1.5 GPa strength [3, 4], ~100% ultimate strain [5]) and thermal properties (~400 W $m^{-1} \cdot K^{-1}$ thermal conductivity [6]), combined with biocompatibility [7] and biodegradability [5, 7, 8]. This makes it potentially useful in practical applications, such as wear-resistant lightweight clothing [9], bullet-proof vests [10], ropes [11], nets [12], bandages [13], surgical threads [14], artificial tendons or ligaments [15], biodegradable food wraps [16], or rust-free panels on vehicles [17]. E.g., in [18], researchers used individual spider silk fibres braided together to create sutures for flexor tendon repair. Enhanced silk mechanical properties could further improve the fatigue strength and lifetime of these structures.

The production of silk is key to the spiders' evolutionary success and has been perfected over 400 million years [7]. Silk is generally described as a semi-crystalline [19], biocompatible [7], composite biopolymer [5], and comprises the amino acids alanine, glycine and serine, organized into semi-amorphous helical-elastic α-chains and β-pleated nanocrystals [20, 21]. From a mechanical point of view, it is considered amongst the best spun polymer fibres in terms of tensile strength [3, 4] and ultimate strain [5], therefore toughness [11], even when compared with the best performing synthetic fibres, such as Kevlar [22]. Silk spinning involves a number of biological, chemical and physical processes [23], leading to its superior mechanical properties.

The natural presence of biominerals in the protein matrix and hard tissues of insects [24], worms [25] and snails [26] enables high strength and hardness (>500 MPa) of teeth [27, 28], jaws [28, 29], and mandibles [30, 31]. Thus, the artificial incorporation of various nanomaterials in biological protein structures to obtain improved mechanical properties should, in principle, be possible. A number of groups introduced inorganic nanoparticles [32], semiconducting crystals [33] or carbon nanotubes (CNTs) [34] on the surface of spider silk fibres, achieving an