Slip knots and unfastening topologies enhance toughness without reducing strength of silk fibroin fibres

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The combination of high strength and high toughness is a desirable feature that structural materials should display. However, while in the past, engineers had to compromise on either strength or toughness depending on the requested application, nowadays, new toughening strategies are available to provide strong materials with high toughness. In this paper, we focus on one of such strategy, which requires no chemical treatment, but the implementation of slip knots with optimized shape and size in the involved material, which is silkworm silk in this case. In particular, a variety of slip knot topologies with different unfastening mechanisms are investigated, including even complex knots usually used in the textile industry, and their efficiency in enhancing toughness of silk fibres is discussed.

1. Introduction

The availability of materials with both high strength and high toughness is greatly desirable in structural applications, although in the past engineers had to compromise and chose one property or the other depending on the application. In fact, strong materials traditionally displayed poor deformation capability and thus low specific energy dissipation potential [1]. However, taking inspiration from nature recent developments in materials science have provided new techniques, that have already overcome the conflict between strength and toughness, such as nacre and bones, with complex structures cooperating at different length scales [2–4]. This concept has been transferred to engineering materials, introducing, for example, weak interfaces with intricate architectures [5] or dispersing fibres in a brittle matrix to form a bridge complementing crack opening and fracture [6].

While all of these solutions require some chemical treatment of the material of interest, in this paper, we considered a different toughening strategy that operates at a micro length scale and enables a significant increase in toughness of as-produced fibres. This follows an idea recently proposed by one of the authors [7] and requires the introduction of a sliding frictional element within the fibre, e.g. a knot. In fact, when the opposite ends of a knotted fibre are pulled apart, a hidden length is revealed through a sliding mechanism that dissipates a huge amount of energy. Basically, this mechanism reproduces the breakage of weak bonds (i.e. sacrificial bonds) in highly coiled macromolecules, which allow the molecular backbone to be further stretched which increases toughness [8].

The fibres considered in this study are of natural origin, as they are extracted from silkworm silk cocoons. In fact, because of its unique combination of biocompatibility, and physical and mechanical properties [9,10], silkworm silk is attracting increasing interest in a variety of biomedical applications, including tissue engineering scaffolds [11–12], drug delivery [13], sensors [14], as well as composites [15]. Such interest motivates the need to further improve the properties of silk, such as its energy dissipation capability (i.e. toughness) [16].
In this paper, the toughness of single silk fibres was increased through the introduction of knots with optimized shape and size. In fact, different kinds of knots can be encountered in everyday life as well as in a variety of fields with studies reporting the application of knots in mathematics [17], polymer science [18,19], colloids [20,21], fluids [22], chemistry [23,24] and biology [25,26]. However, in this paper, we investigated these topologies which enable maximization of toughness without compromising fibre strength. For this reason, as in our earlier work [27], our attention was focused on slip or running knots, which can be unfastened without inducing stress concentration and premature failure in the fibre. In the following, four topologies are considered, involving different unfastening mechanisms and design complexities (some of which are well known in textile industry), with the aim of providing new and feasible tools for optimizing systems where energy dissipation is much sort after.

2. Methods

2.1. Preparation of samples with different slip knot topologies

In the following sections, we report experiments carried out on single fibres extracted from *Bombyx mori* silkworm silk cocoons. In particular, before fibre extraction, as-produced cocoons underwent a standard degumming process [28], consisting of boiling twice with 1.1 and 0.4 g l⁻¹ Na₂CO₃ (anhydrous, minimum 99%, from Sigma Aldrich) water solution for 1 h each time, washing against distilled water and air-drying. In this way, it was possible to obtain silk fibroin fibres released from their natural binding layer (i.e. sericin), which has no load bearing capacity [29].

Then, single fibroin fibres were manipulated by tweezers in order to design knots with the appropriate topology. The knots implemented in our experiments were chosen in order to guarantee that the fibre was highly stressed within a sufficiently large strain interval when its opposite ends are pulled apart (as during a tensile test), but without introducing stress concentration, which could lead to premature failure. Under these conditions, in fact, the introduction of a knot is able to modify the stress–strain curve of the fibres, introducing an artificial plastic-like plateau with a significant increase in toughness [7].

In order for the knot not to affect the fibre strength, it is necessary that the knot can be completely released as the fibre ends are pulled apart. Thus, only slip knots were herein considered. In our earlier work [27], we implemented two different slip knot topologies in single silk fibres, which are known as noose and overhand loop [30] (figure 1a,b). While the noose requires the fibre to be turned once around on itself, the overhand loop requires the fibre to be first folded and then turned around on itself, thus involving a different unfastening mechanism. In fact, in the first case, the knot tends to untie as the fibre ends are pulled apart. Thus, at the beginning, this can be very tight causing the fibre to be highly stressed during the whole tensile test and its toughness to be significantly increased. On the contrary, in the overhand loop, the knot tends to further tie, requiring a very loose initial configuration in order to be released completely, resulting in considerable less toughness in the material. As a consequence, in this work, we investigated and optimized other slip knot topologies that are strictly related to the noose in order to further improve our previous results.

The first topology we considered is an open version of the monkey chain lanyard knot [30], which is well known in the textile industry, as this reproduces a chain stitch of crochet (figure 1c): after a noose is tightened, one thread of the fibre is folded and forced to cross the loop, which ends in a chain of a chain stitch. In some samples, such steps were repeated in order to build chain stitch with four and six chains, respectively. In the following, for the sake of brevity, this knot topology will be referred to as simply a chain knot.

The second topology (figure 1d), which has no common name, requires the implementation of a noose [30]; then, its loop is turned inside the knot, obtaining an X-shaped knot, which is referred to as the X-knot topology in the following.
Figure 2. (a) Stress–strain curve of an unknotted natural fibre with length \( l \) equal to 20 mm, mounted on a paper frame in order for the fibre ends to be 10 mm apart (\( l_0 \)) and with a length of about 10 mm involved in the loop (\( l_{\text{p}} \)) (figure 2a,b).

2.2. Estimation of toughness increase due to knots

The energy per unit mass (i.e. toughness modulus, \( T_u \)) dissipated by an unknotted fibre during a tensile test is related to the area under its stress–strain curve (figure 2a) as

\[
T_u = \frac{1}{m} \int_0^{\sigma_u} F \, dx = \frac{Al}{m} \int_0^{\sigma_u} \sigma \, de = \frac{1}{\rho l_0} \int_0^{\sigma_u} \sigma \, de, \tag{2.1}
\]

where \( m \) is the fibre mass, \( x \) is the displacement at fracture, \( F \) is the applied load, \( A \) is the fibre cross-sectional area, \( l \) is the fibre initial length, \( \rho \) is the volumetric density, \( \varepsilon_f = (l - l_0)/l = x_0/l \) is the fracture strain, \( l_0 \) is the fibre final length and \( \int_0^{\sigma_u} \sigma \, de \) is the area under the stress–strain curve.

If a knot is introduced in a fibre (figure 2b), expression (2.1) has to be modified in order to take into account the length of fibre involved in both the knot (negligible) and the loop, with its toughness modulus, \( T_k \), which can be computed as

\[
T_k = \frac{1}{m} \int_0^{\sigma_k} F \, dx = \frac{Al_0}{m} \int_0^{\sigma_k} \sigma \, de = \frac{1 - k_1}{\rho} \int_0^{\sigma_k} \sigma \, de, \tag{2.2}
\]

where \( \varepsilon_k = x_0/l \) and \( l_0 \) is the initial length equal to the distance between the ends of the fibre, \( \varepsilon_k = x_0/l_0, \quad k_1 = (l-l_0)/l \) accounting for the difference between \( l_0 \) and \( l \) and \( \int_0^{\sigma_k} \sigma \, de \) is the area under the stress–strain curve of the knotted fibre [7].

When the opposite ends of a knotted fibre are pulled apart, the knot causes alternating cycles of loading (the knot is tightened and the fibre is stressed) and unloading (the knot unties, a length of fibre is released from the loop, causing stress relaxation) until the knot loosens completely (figure 2b). In all our tests, the final part of the stress–strain curve of knotted fibres reproduced the stress–strain curve of the corresponding unknotted fibres, showing, in fact, a stress at breakage comparable with the strength of reference samples (without any knots and extracted from a cocoon region adjacent to the knotted fibre) tested separately (figure 2a,b). Moreover, because it is well known that the mechanical properties of silk show significant variability [31], it is preferable to compare the toughness of a knotted fibre with the toughness of the same fibre in unknotted configuration. For this reason, we considered the final part of the stress–strain curve of a knotted fibre as the curve of its reference unknotted fibre. Then, the ratio between the toughness of the knotted fibre, \( T_k \), and the toughness of the corresponding unknotted fibre, \( T_u \), can be obtained with the following expression

\[
\frac{T_k}{T_u} = \frac{Al_0/m \int_0^{\sigma_k} \sigma \, de}{Al_0/m \int_0^{\sigma_u} \sigma \, de} = \frac{\int_0^{\sigma_k} \sigma \, de}{\int_0^{\sigma_u} \sigma \, de}. \tag{2.3}
\]
Tests were carried out at room temperature at a strain rate of 0.002 s⁻¹ by a nanotensile testing machine (Agilent T150 UTM). Following a common approach reported in the literature [29], stress was computed considering each fibre as having a circular cross section, which was evaluated using an optical microscope and scanning electron microscope (SEM). The average diameter of the fibres was 11.5 ± 1.5 μm. All knotted fibres broke at a stress level of about 420 ± 130 MPa, which matches the typical strength of pristine silk fibres.

Figure 2c reports four stress–strain curves, one for each knot topology tested. In all the cases, with respect to the stress–strain curve of a sample with no knots (figure 2a), there is a series of loading and unloading events caused by the fibre sliding into its loop through the knot and related stick-slips, as explained in §2.2. Furthermore, it is interesting to observe that at the end of the test, before the knot loosen completely and the curve collapses into the stress–strain curve of an unknotted fibre, there are some pronounced stress peaks, which correspond to the number of times the fibre was turned around on itself during preparation. In fact, the number of final stress peaks, which is the main factor responsible for toughness increase, is more visible in the case of a chain knot with four and six chains.

As evolutions of the noose, all knot topologies could be firmly tightened and then completely unfastened during the test with quite high-energy dissipation (table 1), depending on the stress plateau value introduced in the corresponding stress–strain curve (figure 2c). In particular, samples with a chain knot with two chains showed a stress–strain curve with a well-defined plastic-like plateau between one-eighth and a quarter of the fracture strength (figure 2c), providing a toughness increase of about 300%, which is comparable to the result obtained with the noose [27]. When the number of chains is

<table>
<thead>
<tr>
<th>knot topology</th>
<th>number of test</th>
<th>toughness increase (%)</th>
<th>strength decrease (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>noose</td>
<td>14</td>
<td>284 ± 43</td>
<td>32 ± 29</td>
</tr>
<tr>
<td>overhand loop</td>
<td>20</td>
<td>118 ± 19</td>
<td>21 ± 37</td>
</tr>
<tr>
<td>X-knot</td>
<td>8</td>
<td>450 ± 107</td>
<td>18 ± 27</td>
</tr>
<tr>
<td>chain knot with 2 chains</td>
<td>11</td>
<td>310 ± 11</td>
<td>7 ± 35</td>
</tr>
<tr>
<td>chain knot with 4 chains</td>
<td>6</td>
<td>150 ± 11</td>
<td>19 ± 27</td>
</tr>
<tr>
<td>chain knot with 6 chains</td>
<td>5</td>
<td>142 ± 18</td>
<td>11 ± 30</td>
</tr>
</tbody>
</table>

(*) Because of variability in the knot tightening procedure, the knot size shows some difference from sample to sample. Thus, when we computed the toughness enhancement provided by each knot topology, we considered an average over three results representative of their optimized behaviour.

where $\int_0^1 \sigma \, d\varepsilon$ is the area under the final part of the stress–strain curve, where the knot is completely released.

However, in case it is not possible to consider the same fibre for comparison, because the final part of the stress–strain curve does not clearly show the behaviour of the fibre in unknotted configuration, we can estimate the toughness increase referring to the toughness modulus of an unknotted fibre extracted from a cocoon region adjacent to that of the knotted fibre in order to limit variations in physical and mechanical properties. In this way, the area under the stress–strain curve of the knotted fibre has to be scaled by the factor $1 - k_i$

$$
\frac{T_k}{T_u} = \frac{(1 - k_i)/\rho \int_0^1 \sigma \, d\varepsilon}{1/\rho \int_0^1 \sigma \, d\varepsilon} = \frac{(1 - k_i) \int_0^1 \sigma \, d\varepsilon}{\int_0^1 \sigma \, d\varepsilon}. \quad (2.4)
$$

3. Results
To evaluate the toughness enhancement owing to knot introduction, we performed tensile tests on more than 50 samples knotted in either of the topologies described in the previous sections. Tests were carried out at room temperature at a strain rate of 0.002 s⁻¹ by a nanotensile testing machine (Agilent T150 UTM). Following a common approach reported in the literature [29], stress was computed considering each fibre as having a circular cross section, which was evaluated using an optical microscope and scanning electron microscope (SEM). The average diameter of the fibres was 11.5 ± 1.5 μm. All knotted fibres broke at a stress level of about 420 ± 130 MPa, which matches the typical strength of pristine silk fibres.

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increased, there is no evident trend in toughness enhancement (table 1). In fact, although some samples with a chain knot with four chains provided significant toughness enhancement of almost 400%, the average value is much lower, being about 150%, which is comparable to the average result provided by chain knots with six chains. However, such values are still greater than that recorded for the overhand loop (table 1).

On the contrary, X-knot topology, providing a higher plateau in the stress–strain curve of the samples, with average values of about one-fifth of the fracture stress (figure 2c) resulting in a toughness enhancement of up to 450% on average (table 1).

4. Discussion

In order to understand the differences in toughness enhancement provided by the investigated knot topologies (table 1), it is necessary to consider the preparation procedure and unfastening mechanism of the knots (figure 3). As we reported in [27], in this case, the lowest toughness enhancement was also provided by the overhand loop. In fact, this is the only topology where the knot tends to further tie as the opposite ends of its hosting fibre are pulled apart. As a consequence, this is able to completely unfasten only when its initial configuration is loose, thus causing low friction against fibre sliding and a consequent limited increase in toughness. On the contrary, the noose can be very tight in its initial configuration, providing a high and wide plateau in the fibre stress–strain curve, which causes the toughness enhancement to be much higher (table 1).

Although the other knots considered in this work, the chain knot and X-knot, both evolve from the noose, they provided different results, which depend on the different sliding mechanisms experienced by the fibre before the knot completely unfastens (figure 3). In this context, the chain knot behaves more similar to the noose, because the chain, which is closer to the loop, tends to open as the fibre ends are pulled apart, thus the fibre can slide easily within the loop and the knot tends to further untie (figure 3). On the contrary, part of the X-knot tends to tie when the fibre is pulled (figure 3). In this case, the fibre appears to be turned twice, but while one turn (which is the closest to the loop) tends to tie, the second turn (on the opposite side) tends to untie as the fibre ends are pulled apart. This means that the knot can always be released, but with significant energy dissipation, causing the fibre to be much more stressed during the test and the toughness induced is more than four times greater than the reference (table 1).

We also investigated the influence of the number of chains on the friction potential of the chain knot. Compared with other knots, chain knots with multiple chains require increasing manipulation, which in turn induces superficial exfoliation in the knotted fibre (figure 2d). This could contribute to enhancing the energy dissipated by friction during unfastening, as the surface of the fibre becomes rougher, but it could also affect the fibre fracture strength, if excessive damage is introduced. From a quantitative point of view, our results show that the introduction of two chains in the chain knot provided approximately a twofold increase in toughness with respect to the average data obtained with four and six chains, which were comparable (table 1). This indicates that in the latter cases, the friction potential was not fully exploited, as it was difficult to guarantee all chains in the knot would be uniformly tightened (figure 2c). Nevertheless, in some cases, we achieved a much more significant increase of almost 400%, meaning that there is still room for further increases, which could be achieved through implementation of a controlled and repeatable production process, as that used in textile industry, where this knot is already commonly applied.

5. Conclusion

In this paper, we compared the effectiveness of different knot topologies to enhance the toughness of single silk fibres. The knots considered herein were characterized by different design complexity, but all had the common feature that they could be completely unfastened when the ends of the fibre were pulled apart. This condition prevented stress concentration in the fibre, which could cause premature failure of the fibre, and enabled dissipation of a significant amount of energy, depending on the knot design. Such results are very promising, because some of the tested knots are already known in the textile industry. Thus, the availability of industrial machinery able to process the knots with high quality and repeatability could easily allow them to be implemented in industrial products requiring energy dissipation capabilities.

Competing interests. We have no competing interests.

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