

Biomaterial applications of silk fibroin electrospun nanofibres



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ABSTRACT

Electrospinning has been very interesting for the recent years and is used since 1994. Today, continuous ultra-fine fibres can be formed with the help of electrical forces to produce various polymer fibres at nanometre scale diameters. Here, it is aimed to discuss this process, for silk fibroin nanofibres and their applications. Silk can be varied in composition, structure and properties. *Bombyx mori* is one of the most studied silk which is widely used as a suture in biomaterial applications. This study focuses on a review of silk fibroin nanofibres and their biomaterial applications. Also, both electrospinning method, the selection of a solvent for the process and SF (silk fibroin) electrospun nanofibre fabrication methods are discussed. Additionally, some studies using SF as biomaterial methods are discussed for tissue engineering applications in this manuscript. It is noteworthy that SF fibres in biomaterials have increased over the last decade due to its excellent mechanical properties, water and thermal resistance, biodegradability and biocompatibility with a variety of end-use in the biomaterials.

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1. Introduction

Silk is very well known in the textile industry for its lustre and mechanical properties. It is produced by cultured silkworms and is a fibrous protein synthesized in specialized epithelial cells that line glands in the class of Arachnida and in several worms of the *Lepidoptera* larvae such as silkworms, spiders, scorpions, mites and flies [1].

Silk fibroin polymers contain protein series and are responsible for cocoon and web formation, nest building, etc. [1,2]. As they have mostly β -sheet structures consisting of short side chain amino acids in the primary sequence, they permit tight packing of piled sheets of hydrogen bonded anti-parallel protein chains. Because of both large hydrophobic and smaller hydrophilic areas they allow to promote the assembly of silk which is very good in strength and resiliency [3]. In the literature, there are several researches [4–6] on *Bombyx mori* (Fig. 1) to study the properties of these silk proteins for biomaterial purposes.

Silk fibres from *Bombyx mori* (*B. mori*) are generally 10–20 μm in thickness and each fibre is in fact duplet of two individual fibres. Each of these fibres has its own silk coating (sericin) and an inner core (fibroin). Fibroin is consist of parallel fibrils around 100–400 nm and has excellent mechanical properties which can be compared with some of the other fibres seen at the Table 1.

On the other hand, biomaterials are one of the extensively studied subjects in both tissue engineering and in nano technological related fields i.e. textiles, physics, biology. Their mainly functions are allowing cell migration, adhesion, differentiation, degradation at some rate to allow cells to deposit new extracellular matrix (ECM) and regenerate functional tissue, some may also need to be mechanically supportive and superior, ready to solvent processing and most generally have to be biocompatible and they do cause little or no reaction to one's immunity.

The aim of the present study is to give a brief review on silk fibroin nanofibres, their fabrication method by electrospinning process and their biomaterial applications.

2. Electrospinning

2.1. Processing

Electrospinning was patented by Anton Formhals in 1934 and is a combination of two techniques which are electro spray and spinning of fibres [8]. Fig. 2 displays a diagram of an electrospinning apparatus; it includes a capillary tube with a needle or pipette (1), a high power voltage supply (2) and a collector (3).

A high electric field is both applied to the capillary tube, which has a melt or a polymeric solution, and to the collector. The collector and the capillary tube are kept a relatively short distance from each other. Copper plates, aluminium foil, rotating drums can be used as a target for the collection of nano fibres during the electrospinning process [10–13].

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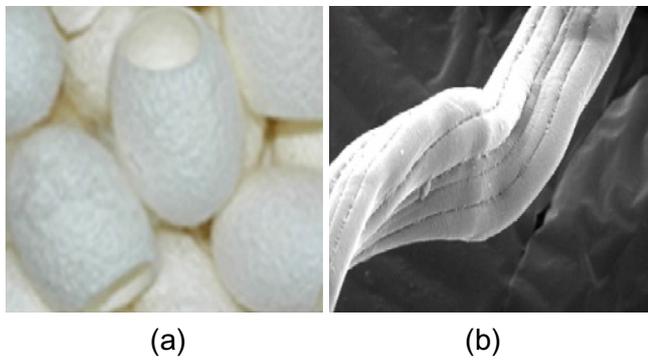


Fig. 1. (a) *Bombyx mori* cocoons and (b) triangular cross section of a silk fibroin fibre (25 µm) [6].

Table 1
Typical properties of silk and some other fibres [3,7].

| Fibre type | Diameter (µm) | Specific gravity | Strength (GPa) | Strain to failure (%) | Young's modulus (GPa) |
|------------------|---------------|------------------|----------------|-----------------------|-----------------------|
| Silk (silk worm) | 12 | 1.40 | 0.40 | 25 | 8 |
| Cotton | 10–27 | 1.54 | 0.60 | 7 | 8 |
| Poly-ester | 15 | 1.38 | 0.80 | 15 | 15 |
| Kevlar 49 | 12 | 1.45 | 3 | 4.5 | 135 |
| Nomex | 15 | 1.38 | 0.64 | 22 | 17 |

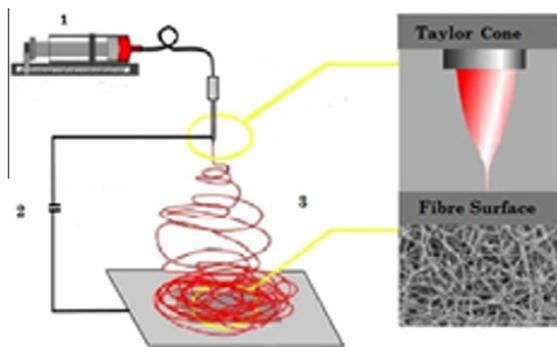


Fig. 2. Diagram of a typical electrospinning apparatus [9].

The polymer solution is held by the pipette and when a sufficiently high voltage is applied to the pipette, the body of the liquid becomes charged. Then electrostatic repulsion counteracts the surface tension and the droplet is stretched; at a critical point a stream of liquid discharges from the surface which is a conical protrusion known as the *Taylor cone* [14]. For a few centimetres, an approximately straight jet emerges from the cone for a while and then it emerges into a transparent and conical shape. Fig. 3 shows a photograph of a Taylor cone where a fibre being electrospun from it. During the conically movement of the jet bending instabilities are accomplished and its field is directed towards the target which has an opposite electrical charge. Ultimately, it takes the jet to reach the target and finally the solvent evaporates and dry polymer fibres are deposited [15].

2.2. Applications

Many applications are desired to have aligned or specific arrangements of piled up nanofibres. These alignments can be achieved by various methods, i.e. patterned electrodes [17], disc

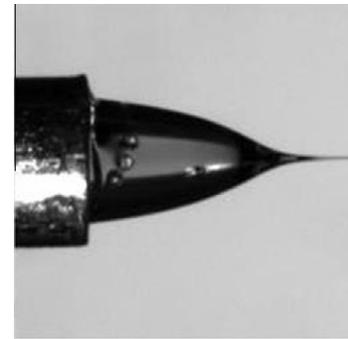


Fig. 3. Taylor cone [16].

collectors [18] etc. By doing this and other parameters such as molecular weight and their distribution, solubility, viscosity, surface tension, electrical conductivity, solution feed rate, substrate properties, relative humidity etc. can affect the morphology of the electrospun fibres [19] and their nano-effects [20], which is known as increment on the surface area, will enhance the properties of the product. According to both parameters that are chosen and the demands for special end-uses, a particular consumer application can be manufactured. Nanofibres in biomaterials and biomedical fields have displayed numerous applications like enzyme immobilization [21], drug release [22] and tissue engineering [23–25] which both are closely related, wound dressing [26,27], nanomats [28,29], antibacterial materials [30], and vascular grafts [31]. Some of these applications are given in Section 3.1 of Silk fibroin nanofibres.

3. Silk

Silk is an ancient and the only natural filament fibre which is used for thousands of years and for the year 2011, China (126 ktons), India (20.4 ktons), Viet Nam (7.05 ktons), Romania (2.1 ktons), Thailand (1.6 ktons) and Uzbekistan (1.2 ktons) are the six major silk producers in the world [32]. Silk, is a fine, strong continuous fibroin filament produced by the larva of certain insects especially the cultured silkworms constructing their cocoons. Raw silk fibre has natural impurities such as wax, carbohydrates, inorganic matter and pigment less than 3% wt of a fibre. In a composition of a silk fibre, fibroin content is about 70–80% and the content of sericin, which is silk gum and usually removed in processing, is about 20–30% [33].

There are two main types of silk fibre, cultivated and wild; they differ in diameter, cross-sectional shape and in fine structure. Its length is about 300–600 m [34]. Because of its beauty, its handling and its high cost, silk is also known as a luxury fibre and hence it remains its use both in various textiles i.e. fabrics, underwear, socks, leggings and has a great place for the fashion designers' collection. But more recently, silk has started to fascinate nano technologists in their studies which consist of fibroin [35–41] in biomaterial applications. Before discussing some of these studies and their applications which are mentioned in the following sections, here is a method discussed on processing for silk fibroin.

3.1. Silk fibroin nanofibres

As it is already mentioned that silk fibroin (SF) is a natural protein fibre and it has been investigated thoroughly for biomaterial applications. Briefly, silk process involves the selection of a proper silk source, e.g. *B. mori* or a wild silk, silk degumming to isolate sericin from fibroin fibres, fibroin dissolution and fabrication of new

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