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Original Research Paper

Effect of multi wall carbon nanotubes on characteristics and morphology of nanofiber scaffolds composited of MWNTs/silk fibroin

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ABSTRACT

Composite of multi wall carbon nanotubes (MWNTs) and silk fibroin were electrospun to nanofiber scaffolds with average diameter ranged from 46.2 to 100 nm. The effect of increasing the percentage of the MWNTs was evaluated on properties, characterizes and morphology of composite nanofiber scaffolds. Solution concentration, electric field, distance of needle from collector and flow rate were optimized for electrospinning. Optical and scanning electron microscope were used to study the morphology and diameter of composite nanofibers. The properties and characterizes were considered by using the FTIR spectroscopy, X-ray and Raman spectroscopy in addition, the electrical conductivity was measured utilizing Four-Point Probe method. Results showed that augmentation of the MWNTs had a small effect on the nanofiber surface. A growth was seen in the composite nanofiber diameter by increasing the MWNTs. Chemical interaction was not happened between MWNTs and silk fibroin based on FTIR spectroscopy and X-ray analysis also, crystallization of composite nanofibers grew by adding MWNTs. Raman spectroscopy proved that MWNTs were incorporated in the silk fibers. The electrical conductivity of composite nanofiber scaffolds was increased by increment of the MWNTs.

1. Introduction

Natural fibers have nanometric or submicrometric dimension and there are several techniques to produce scaffolds with components in this dimensional range [1] the electrospinning (ES) is a good technique to product nanofibre scaffolds that are made of several different polymers [2–5]. This approach has attracted attention because of it is simple, inexpensive and can be scaled-up, also it is possible to produce micrometers fibers to nanometers in diameter by adjusting of different parameter of electrospinning process [6]. This technique includes a polymer solution that is pushed through a spinneret using a syringe pump with a controlled flow rate. High voltage (usually up to 30 kV) is applied and solid fibers are collected on a collector surface [7].

Thus scaffolds with desirable geometries and properties can be obtained with selecting suitable material/composite solutions and by use of processing various parameters [8].

Protein-based polymers such as silk have been used in tissue engineering and textile materials because of their good biocompatibility and suitable structural properties [9]. B. mori silkworms have been farmed for thousands of years, the triangular cross section and 10–20 μm size of *Bombyx mori* fibers remain unchanged, recently researchers have investigated that silk is potential for biomedical applications because of its specific biological properties that include good biocompatibility, good oxygen and water vapor permeability, biodegradability, and minimal inflammatory reaction [10–12]. Silk fibers are composed of two protein microfilaments that located inside of glue-like glycoprotein coating (Sericin) [13,14]. Sericin can be removed by degumming treatment and it constitutes 25–30% of the fiber weight [15–17]. Fibroin filaments are composed of nanofibril bundles that are aligned with the fiber axis. These nanofibrils are composed of three complex protein components. Part of large protein is heavy chain fibroin (H chain) that is connected to a small protein or light chain fibroin (L-chain) by disulfide bonds and third part is small glycoprotein protein (P25) that is linked via non-covalent hydrophobic interactions [18–20]. *Bombyx mori* silk fibroin is a biomacromolecule protein that composed of 5507 amino acid and is consisting of repeated sequences of $(\text{Gly-Ala-Gly-Ala-Gly-Ser})_n$. Many researchers used silk fibroin protein as biomaterials in the forms of films, three-dimensional scaffolds, hydrogels, electrospun fibers and microspheres [21].

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Silk is known as strongest fiber in nature with high strength up to 4.8 GPa, also another their properties are lightweight (1.3 g/cm^3) and remarkable toughness and elasticity (up to 35%) [22]. In addition to silk is thermally stable up to about 250 °C, therefore processing over a wide range of temperatures is possible [23]. The required tensile strength and energy to break silk is higher than synthetic high-tenacity fibers like Kevlar 49 [24] you can see more details on the structure, mechanical properties and biocompatibility of silks in recent reviews [25–29].

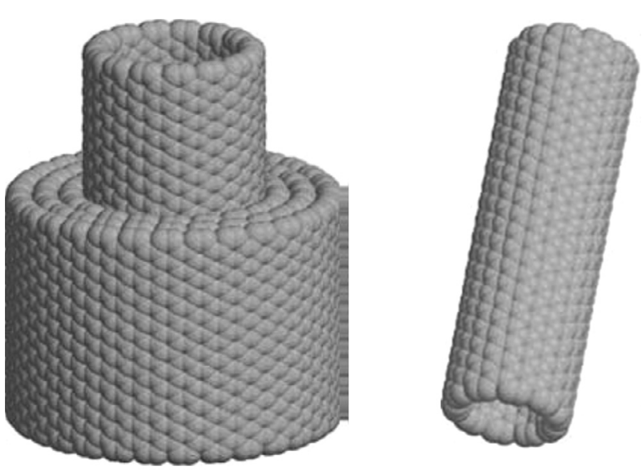
Silk fibers are insoluble in most solvents such as ethanol, water, dilute acids, but it is soluble in highly concentrated sulfuric acid, formic acid, hexafluoroisopropanol (HFIP), calcium nitrate or LiBr solutions [30,31].

Among the useful techniques for production of silk fibroin nanofibers, electrospinning is a very attractive opportunity to produce of nanoscale fibers also 2D and 3D scaffolds from natural and synthetic sources with diameters of 2 nm to several micrometers [32–35].

Fiber in nanoscale with smooth surfaces, almost circular cross section, and proper biocompatibility can be made from electrospinning process of regenerated silk fibroin. According to researchers, electrospun silk fiber had the mechanical properties more weak than the natural fiber [36]. The difference in mechanical properties of the nanofibers and natural silk fiber may be because of the processing steps during in the nanofiber formation that cause differences in crystallization and molecular orientation of the chains [37–42]. It is a necessary to improve the mechanical properties of the electrospun fibers in order to their different application. Getting to silk fibers mechanical properties is possible by drawing, after treatment or adding one material to solution of electruspun to improve desired properties.

Carbon nanotubes (CNTs) are one atom thick layers of graphite rolled into a cylinder [43]. Fig. 1 Multi wall carbon nanotubes (MWNTs) has attracted much attention due to its light weight, flexible, elongation of 6–30% and its weird properties, such as excellent electrical, mechanical, thermal properties, and also it is so cheaper than single wall carbon nanotubes (SWNTs) [43–46]. Adding small amounts of CNTs, with dispersions method to polymer solution, can improve the mechanical strength and electrical conductivity of the polymer composites in comparison with the primary polymer significantly [47,48].

Electrospinning offers an alternative approach for producing submicrometer fibers from protein fibers. Silk is a well described natural fiber that produced by the silkworm, *Bombyx mori* and it is interested in the use as proteins in biotechnological materials and biomedical applications, originates [44]. Recently, CNT-filled nanofibrous membranes have been produced by electrospinning to improve their performance characteristics [44].



(a) **(b)**

Fig. 1. (a) Multi-walled carbon nanotube (MWNTs), (b) single-walled carbon nanotube (SWNTs) [42].

The main aim of this study is to consider the effect the MWNT's on the silk fibroin nanofibers. Optical and scanning electron microscope, the FTIR spectroscopy, X-ray analysis, Raman spectroscopy and Four-Point Probe method were used to study the morphology and characterizes of composite nanofibers, respectively.

2. Experimental

2.1. Materials and methods

Silk fibroin, protein was isolated from silk of B. mori, was prepared from north of Iran, following standard extraction procedure [49]. Modification of silk fibroin (SF) was prepared by degumming silk twice in Na_2CO_3 (2 g/l) and anionic detergent (10 g/l) solution at 100 °C for 30 min and then rinsed with distilled water several times to remove sericin from the silk fibers, finally it dried in 40 °C completely. All reagents were purchased from the Merck Company, unless otherwise mentioned. Formic acid (98%) and calcium chloride (100%) were purchased from the Merck Company too.

2.2. Preparation of silk fibroin solution from Bombyx mori silk

Degummed SF was dissolved in a triplex solvent system of $CaCl_2–CH_3CH_2OH–H_2O$ (226.4 g, 364 g, and 284 ml respectively for 35 g of degummed SF) at 70 °C for 4 h, then solution dialysis was carried out with cellulose tubular membrane in distilled water for (48–72 h) at 23 °C, after dialysis the SF solution was filtered and lyophilized to obtain the regenerated SF sponges. The dialyzed fibroin solution was frozen for 24 h at −20 °C and then lyophilized to produce sponges. The SF solutions were prepared by dissolving the silk fibroin in 98% formic acid for 3 h.

2.3. Preparation of SF/MWNTs composite solution

Nanocomposite scaffolds was carried out by electrospinning of regenerated silk in formic acid along with multi wall carbon nanotubes, purchased from Neutrino Company with purity over 95%. MWNTs were dispersed in the required amount (2.5–10) wt% in 2 cc of formic acid by sonication for 10 min. The regenerated silk (13%w/v) was added to this mixture and sonicated for 10 more min again, finally solution was mixed with magnetic stirrer for 3 h.

2.4. Preparation of silk nanofiber and SF/MWNTs composite nanofiber

Silk fibroin was prepared as described above; electrospinning was performed as described in previous studies [50,51]. The SF nanofiber matrix was prepared by electrospinning at the concentration of (9–15) w/v%. The electrospun SF nanofibers were collected on an aluminum foil covered metallic plate which was placed at a distance of 7–10 cm from the syringe tip. electrospinning done at voltage of (18–26) kV and the flow rate of the polymer solution was (0.01–0.04) ml h^{-1}.

For preparation of composite nanofibers, syringe was filled with 2 ml of a MWNTs/silk/formic acid solution and was placed at a distance of 10 cm from collector, then electrospinning done with flow rate of 0.04 ml/h, at the voltage of 22.0 kV.

2.5. Nanofiber characterization methods

Properties of the scaffolds were characterized by Scanning Electron Microscopy (SEM), FT-IR, XRD and Raman spectroscopy

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