Dispersion characteristics of silk fibroin protein polymer

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ABSTRACT

Silk is a natural protein fiber and is widely used in textile technology. Apart from textile technology, silk is preferred in many fields and applications such as biomedical because of its superior advantages. In this study, the fibroin silk solution was used as a biomaterial. The refractive indices of silk fibroin (SF) protein polymer were obtained and the refractive index dispersion of the SF protein polymer was analyzed in detail.

ARTICLE INFO

1. Introduction

Silk is a natural protein fiber spun by a variety of insects in nature and it has been used for thousands years as a textile for luxury clothing because of its texture, mechanical strength and optical luster [1]. Silk has been used in different applications for a long time due to its properties such as texture, strength, and shine, as well as its importance in culture, economy and science [2]. While silk is used in many industrial areas due to its mechanical properties, it has also been used in biomedical areas due to its polymer structure [3, 4]. In the last two decades, tissue engineering studies have been conducted on silk fibroin (SF), one of the two main proteins of silk [5]. Fig. 1 indicates the various applications of SF for bone tissue engineering [1].

Successfully integrated with biomaterials, SF can create advantages that are compatible with different materials, as well as advantages such as low cost, biocompatibility, biodegradability and renewability [6]. Due to the mechanic durability and high transparency of the SF there are studies explaining its use in optical and photonic, electronic and optoelectronic applications [7, 8]. SF has the function to easily provide biological integration with vehicles with optical properties such as thick films, ultrathin films, nanoscale and large diameter fiber [9]. Thus, bioelectronics provided advantages in optofluidics, organic light-emitting transistors and micro / nanophotonics researches [10-13]. One of the excellent features of SF is that it can be prepared with multi-layer options such as fibers, yarns, films, hydrogels and porous materials, as shown in Fig. 2, since their aqueous solutions can be easily prepared. SF is used in the production of optical devices such as diffractive optical elements (DOEs) and light emision diodes (LEDs). Large refractive index (about 1.54) is attractive for DOEs options [14].

2. Results and Discussion

The refractive index is one of the most important optical parameters for the characterizations used in the glass, polymer and plastic industries [15]. Parameters such as reflection and permeability are needed to calculate the

refractive index [16]. Different methods and techniques were used for these calculations. One of them is the ray tracing approach, which aims to find reflection and

transmittance without absorbance [17]. Multiple beam incompatible reflection equation:
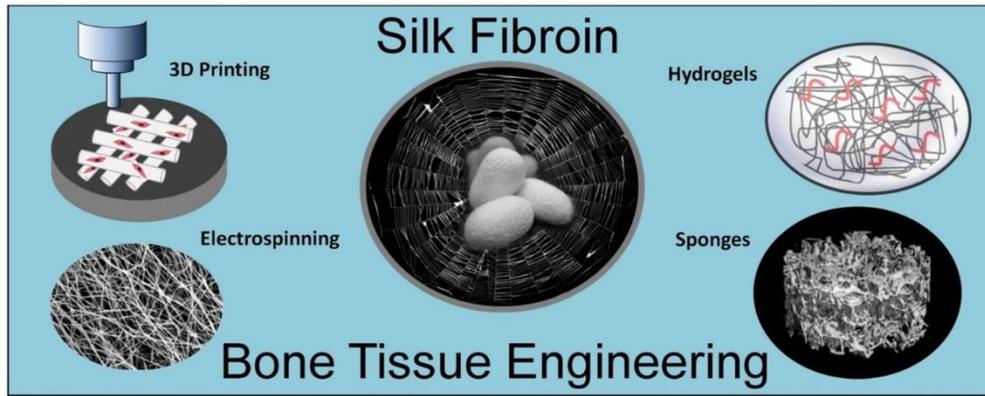
Fig. 1. Silk fibroin as biomaterial for bone tissue engineering [1].
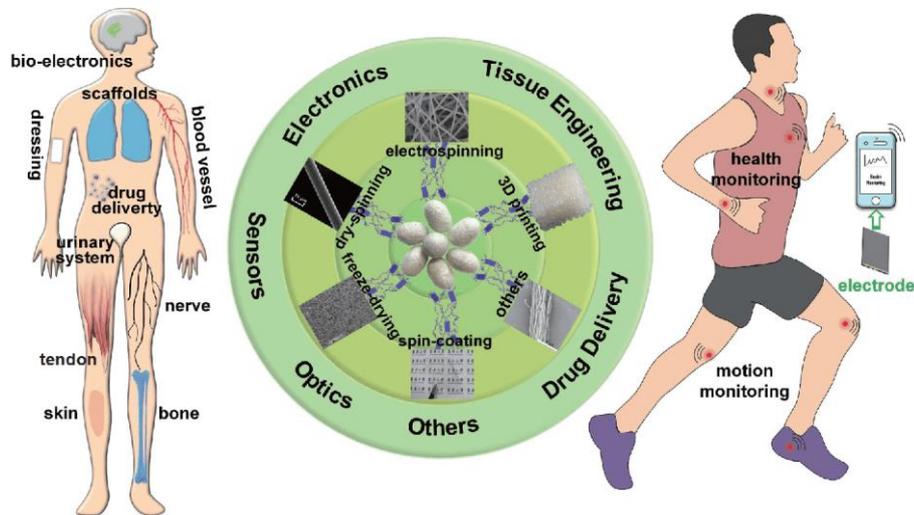
Fig. 2. Schematic diagram of the structure, processing, forms and applications of silk materials [14].

$$R = R_{as}\left(1 + \frac{\eta^2 T_{as}^2}{1 - \eta R_{as}^2}\right) \quad (1)$$

where T_{as} is incompatible transmittance.

$$T = \frac{\eta T_{as}^2}{1 - \eta^2 R_{as}^2} \quad (2)$$

Spectral reflection and transmittance can be used to find refractive indices. From Eq. 1 and 2;

$$k = \frac{\lambda}{4\pi t}\ln\left[\frac{T\left\{\left[2+T^2-(1-R)^2\right]-\left[\left(2+T^2-(1-R)^2\right)^2-4(2-R)R\right]^{1/2}\right\}}{\left\{2(2-R)R+\left\{\left[2+T^2-(1-R)^2\right]^2-4(2-R)R\right\}^{1/2}-(2-T^2)-(1-R)^2\right\}}\right] \quad (3)$$

After performing the necessary operations, the reflection of the interface between the air and the surface in the case of normal incidence is given as follows:

$$R_{as} = \frac{(1-n)^2 + k^2}{(1+n)^2 + k^2} \quad (4)$$

Thus, the reflection of the SF protein polymer is obtained as seen in Fig. 3.
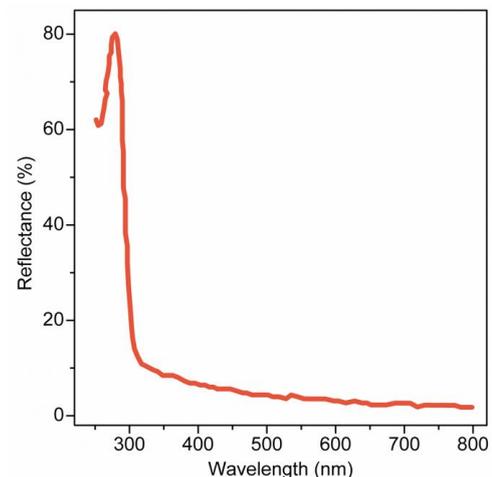
Fig. 3. The reflectance curve of the SF protein polymer.

One of the important parameters of optical materials is closely related to the refractive index (n), electronic polarization of ions and the local area within the materials. Refractive indexes of optical materials are important for optical device design and applications in integrated optical devices [18, 19]. High refractive index is often used in many optical technologies such as solar cells, Bragg grids, photonic crystals to increase the optics and performance [20]. The complex optical refractive index is given as follows;

$$\tilde{n} = n(\omega) + ik(\omega) \tag{5}$$

where n, real part, k imaginary part of complex refractive index. To find the refractive index, the following equation is used;

$$n = \left\{ \left[\frac{4R}{(R-1)^2} - k^2 \right]^{1/2} - \frac{R+1}{R-1} \right\} \tag{6}$$

where R is the reflection of the SF protein polymer. The refractive index (n) dispersion plays an important role in optical communication and designing of the optical devices. Therefore, it is important to determine dispersion parameters of the solutions. The refractive index dispersion was evaluated using the single oscillator model due to normal dispersion behavior. Fig. 4 shows the curve of the refractive index with respect to angular frequency.
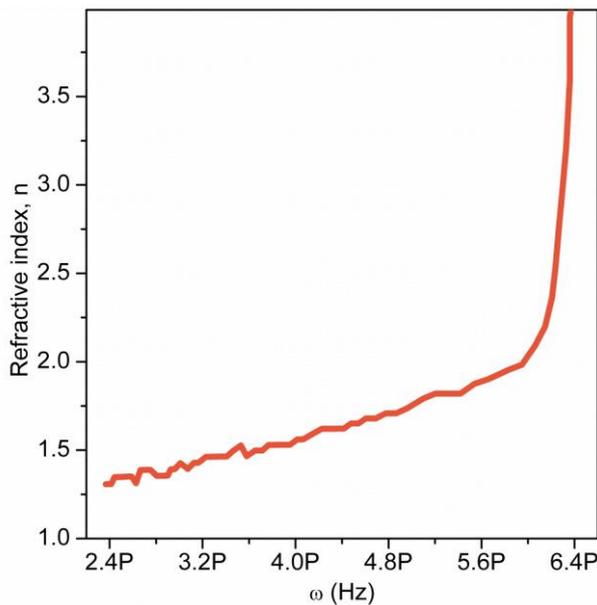
Fig. 4. Curve of refractive index against frequency.

Wemple-Di Domenico (WDD) equation is used for refractive index dispersion. The refractive index distribution can be analyzed with the WDD single oscillator model [21,22].

$$n^2 - 1 = \frac{E_d E_o}{E_o^2 - E^2} \tag{7}$$

Single oscillator energy (E_o) simulates all electronic stimuli, while dispersion energy (E_d) is a measure of the optical density between the bands and describes the average strength of the optical transitions between the bands. In this model, the dielectric state is examined at transitions below the optical space, E_o and E_d are parameters related to the imaginary part of the complex dielectric constant. WDD dispersion parameters E_o and E_d values were obtained by using Eq. (7), as 1,604 eV and 5,575 eV, respectively. E_o is the parameter related to the optical band gap, while E_d is the parameters related to ionicity, anion valency, coordination number [23,24]. The dispersion plays an important role in the research for optical materials in designing optoelectronic devices [25]. The following equations are used to find the moments of the imaginary part of the optical spectrum M_{-1} and M_{-3} of the SF protein polymer;

$$E_o^2 = \frac{M_{-1}}{M_{-3}} \tag{8}$$

and

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \tag{9}$$

M_{-1} and M_{-3} values were calculated for SF protein polymer and M_{-1} moment value (3.476) while M_{-3} moment value (1.352 eV^{-2}) was found. These values are the measure of the average bond strength. Optical moment values are associated with macro coverage amounts, such as the effective dielectric constant and the number of effective valence electrons in the investigated materials [26,27].

The optical oscillator strength (f) in the optical transitions is that the electron absorbs the photon during the transition. Oscillator strength is a measure of how the optical material interacts with radiation, as the transition rate is linearly increased by the square (f^2) of the oscillator force. f is given by the formula [28]:

$$f = E_o E_d \tag{10}$$

The optical oscillator strength (f) 8.941 eV^2 was determined.

3. CONCLUSION

We investigated the refractive indices and dispersion characteristics of silk fibroin protein polymer. This SF polymer exhibits maximum reflectance at about 280 nm. The refractive index dispersion of the SF polymer exhibits normal dispersion properties. Thus, Wemple-Di Domenico dispersion parameters were obtained. The results obtained

show that compatible refractive indices are obtained and silk fibroin protein polymer can be used in reflectance-based nanofiber and optoelectronic devices.

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