Green Degumming Processes of Silk

Subjects: Engineering, Chemical

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Traditional textile degumming processes, including soap, alkali or both, could bring such problems as environmental damage, heavy use of water and energy, and damage to silk fibroin. The residual sericin may influence the molecular weight, structure, morphology and properties of silk fibroin, so that degumming of silk is important and necessary, not only in textile field but also in non-textile applications.

silk filaments fibroin sericin green degumming enzyme

1. Introduction

Silk, generally known as the "queen of fiber", has not only been used in the textile field but also in biomedical field [1][2][3]. In fact, silk can be produced by the species from Arachnida or Lepidoptera, such as mites, butterflies and moths [4]. Among such kinds of silks, those from the domesticated silkworms (*Bombyx mori*) are used mostly. Unless otherwise stated, silk in this paper points to the *Bombyx mori silk*.

The silk is mainly composed of two kinds of proteins, the inner insoluble fibrous protein, which is usually named fibroin, and the outer global hydrophilic protein, named sericin [2][5]. Due to big differences, such as appearance, solubility, amino acid composition and amount of reactive groups, silk fibroin and sericin usually needs to be separated before further processing.

In textile fields, in order to obtain silk fibroin filaments with an excellent hand, elegant luster, high capillary rise height, a process called degumming (also called scouring) is necessary [6][7]. Sometimes, when the whiteness of silk fibroin filaments is not good enough, bleaching is applied [6]. After degumming, silk fibroin filaments can be dyed, printed or finished for textile applications. While in non-textile field, purified silk fibroin can be obtained through a simple degumming process, such as alkali degumming and boiling water. After that, silk fibroin can be further processed to film, sponge, scaffold, hydrogel, and non-woven mats for non-textile applications.

2. Types of Green Degumming

Traditional degumming processes could cause problems such as environmental damage, heavy use of water and energy, and damage to silk fibroin.

2.1. Enzyme Degumming

Enzymes, usually composed of amino acids, are one kind of large biological molecules biocatalyst, which can be widely used in textile field, such as pretreatment of cotton, degumming of silk, bleaching and shrink proofing of wool due to their mild conditions of temperature and pH, high specificity and efficiency, reduced water and energy consumption [8][9] and little damage to silk fibroin [10][11][12][13]. It is reported that more than three quarters of industrial enzymes are hydrolytic in action, while protein-degrading enzymes count for two over five [8]. Among protein-degrading enzymes, proteases are the largest group with animal, plant and microbial sources which could be active under alkaline, acidic and neutral conditions [9].

In order to completely separate sericin from silk fibroin without obvious hydrolytic damage to the latter, Li et al. [11] used papain to degum *Bombyx mori* silk filaments under nearly neutral conditions. They found that sericin was completely removed, and silk fibroin still had a high molecular weight when the concentration of papain reached 3.0 g/L. This could be explained because, here, papain specifically breaks the binding sites between L-arginine or L-lysine residue and another amino acid residue in sericin, resulting in the clean and smooth surface of silk fibroin. Furthermore, they also found higher tensile strength using papain degumming than that under the traditional degumming process with sodium carbonate. They further prove that papain is a good alternative for degumming silk.

Besides, Promboon et al. [14] selected a commercial grade stem bromelain as the effective degumming agent for Mai 1 silk filaments. The results indicated that the fibroin was not damaged, and the silk fabric was provided with good physical properties, such as tensile strength with bromelain degumming method, compared with traditional sodium carbonate degumming method. Although bromelain is shown as a good biocatalyst, active pH range and corresponding mechanism of action were not reported.

Freddi et al. [15] picked up four such commercial proteases for silk degumming process including oxidative-stable endopeptidase, bacterial high alkaline strain, papain and aspergillus pepsin I. They found that only alkaline and neutral proteases were effective for the degumming of silk filaments, while the acid protease was ineffective under the experimental conditions adopted. Further study showed that even though the degumming ratio reached 25%, there was almost no sericin remaining on the warp of silk filaments while still some sericin deposited on the highly twisted weft, indicating that texture of silk could also influence the effect of degumming.

Chim-anage et al. [16] screened and isolated an extracellular serine protease of *Bacillus* sp. C4 SS-2013 (C4), used for the degumming of silk filaments. They found that the protease has a high specificity to sericin protein, and even at incubation for three days, the silk fibroin was not damaged while the sericin was completely removed. Furthermore, this protease was easily concentrated and suitable for longer storage at low temperatures. Although C4 is a promising alternative for degumming silk, whether it can be in large-scale production and for wide applications is still unknown.

Apart from the above teams devoted to studying the biological degumming of silk filaments with enzymes, other groups also promote this art [17][18][19][20][21][22][23][24][25][26][27]. It is anticipated that with the discovery, screen and isolation of more enzymes suitable for the silk degumming, corresponding environmentally friendly and green degumming processes will be developed and make silk degumming flourish.

2.2. CSCF Degumming

CO_2 supercritical fluid (CSCF) can be considered as the CO_2 above its critical temperature (Tc, generally 304.25 K) and critical pressure (Pc, generally 7.38 MPa), under which CO_2 shows some unique properties, such as appropriate viscosity and diffusivity like gas, appropriate density and solvating properties like liquid, making it as solvent candidate so that CSCF can be applied in many fields [28][29][30][31][32][33][34][35][36][37]. In textile fields, CSCF is usually used for dyeing due to its environmentally friendly nature for the replacement of organic solvents or water and easy recovery and recycling [28][29][30], compared with traditional dyeing process. Besides the application in dyeing synthetic or natural fibers, CSCF can also be used for pretreatment of cotton [34][35] and flax fibers [36][37]. However, up to now, little information on degumming of silk using CSCF was reported.

Lo and his collaborator [32][33] conducted a series of studies on silk degumming using CSCF. The whole process includes the acid pretreatment of silk filaments with the aid of a surfactant, treatment with CSCF in the container under appropriate conditions and post-treatment using ultrasonic method. In this way, the cleaned silk fibroin filaments could be obtained. The mechanism could be explained that after pretreatment with citric acid or tartaric acid, the silk filaments carry positive charges due to both the isoelectric point (pI) of silk fibroin (3.6) and sericin (3.3) higher than experiment pH (2–3) [31][32][33]. Since citric acid or tartaric acid contains a carboxylic acid group, they can interact with the hydrogen ion (proton) on the surface of silk sericin to damage the amino acid structure of the sericin and with the help of a surfactant, a hydrophilic site will be created under CSCF. Then sericin can be easily removed from silk filaments by ultrasonic post-treatment. Although silk degumming using CSCF is efficient and can keep silk fibroin less damaged than conventional ammonium hydroxide degumming method, the complicated process is required. Hence, the development of easy and efficient degumming process of silk filaments with less damage to silk fibroin by CSCF method is quite necessary.

2.3. Acid Degumming

Besides enzymes and CSCF degumming, degumming of silk filaments with citric acid can also be considered an environmentally friendly degumming process due to the biodegradable nature, reduced water consumption and less damage to silk fibroin [38][39]. Citric acid (CA) is a mild organic acid with good biodegradability, safe and pleasant taste, high water solubility, good chelating and buffering properties which has been widely used in food, cosmetic, chemical and biomaterials fields [38][39][40][41].

In biomaterials field, citric acid acts as a green cross-linker for various applications, such as tissue engineering, cancer therapy, wound dressings [42][43]. It is interesting to point out that, in textile field, citric acid was first used as the cross-linker for the textile finishing instead of pretreatment [44][45][46][47].

Tsukada et al. [48] applied different concentration of citric acid for the degumming of silk filaments to study the effect of citric acid treatment on structure, morphology and properties of silk filaments. They found that molecular conformation and the crystalline structure did not change after degumming with citric acid, and almost no sericin remained on the surface of silk filaments with 30% citric acid when the total weight loss reached 25.4%, together with good tensile properties. They stated that citric acid degumming can be an alternative for industrial application. However, the pH of degumming bath containing 30% citric acid was not reported and whether such conditions can be suitable for industrial applications is still unknown.

2.4. Steaming Degumming

As one kind of efficient processing methods for the biomass conversion, the used steam has higher efficiency of heat transfer due to its greater heat capacity and not decreasing the moisture content of treated objects like wood, compared with hot air [49][50][51]. In the textile wet process, steam treatment is often used for padding dyeing, printing and finishing process [52][53][54][55][56].

Similar to CSCF degumming, the steam process for textiles seems to be the environmentally friendly due to no harmful chemicals use and low water consumption. However, litter information on steaming process for pretreatment of silk filaments. Recently, Zhu et al. [57] showed a routine of silk degumming by steam treatment without aid of any chemicals. They used a modified pressure cooker as the steam treatment apparatus. Ultrasonic treatment and following washing process was applied after the steam degumming. The results show that sericin was almost completely removed under optimal conditions, and some physicochemical properties of the silk fibroin filaments did not change. Energy efficiency analysis indicates steam treatment is an efficient technique for raw silk degumming with lower processing cost and without chemical used, compared to the conventional chemical degumming methods. Since steam degumming for raw silk filaments can be considered as an environmentally friendly and green process, large scale of steam degumming of silk filaments for textile applications and non-textile applications is worthy of further investigation.

2.5. Ultrasonic Degumming

In biomedical applications, sonication becomes a useful tool to control the rapid sol-gel transition of silk fibroin to form hydrogel, and to regulate the protein structure to obtain protein-base materials [58][59][60]. In textile field, ultrasonication is also widely used for dye extraction, textile dyeing due to the ability of sonication of breaking aggregates of dyes, breaking the fiber-dye interfacial layer and increasing the swelling of fiber to accelerate their diffusion into the fiber [61][62][63].

Besides, sonication is also often seen in textile washing, including pretreatment and post-treatment [57][64][65][66]. With this technique, fewer chemicals are used and washing effectiveness is improved [64][65][66], therefore, ultrasonication can be thought to be an environmentally friendly and green process.

However, up to now, there is less information on degumming of silk filaments with sonication [67][68]. Recently, Arami et al. [67] applied different degumming techniques based on ultrasonication for raw silk yarns. In short, such techniques can be divided into two groups: one-bath degumming process and two-bath process, and the former group includes ultrasound degumming, ultrasound–enzyme degumming and traditional soap-alkali degumming, while the latter includes ultrasound and soap degumming, ultrasound and enzyme degumming, ultrasound and enzymes mixture degumming. The results show that the optimal degumming process is two-bath based ultrasound and enzymes mixture degumming, with significantly increased degumming efficiency perhaps due to their synergetic effect. Such a sonication-based environmentally friendly degumming process is very meaningful and important because it can help other research teams try different combinations of degumming process, develop many eco-friendly degumming processes and achieve a wide range of applications. Similar to the work by Arami, Li et al. [68] applied the citric acid, sodium carbonate and papain as the degumming agents for the silk filaments reeled from silk cocoons with the aid of ultrasonic treatment at four different frequencies. They found that a higher degumming rate was obtained degummed by ultrasonication at a lower frequency than at a higher frequency. They also found that papain degumming was more effective than citric acid and sodium carbonate with higher degumming rate. With increasing degumming temperature and time, less sericin was remained on the surface of silk filaments with papain degumming, resulting in smooth and clean surface, however, this may decrease silk whiteness. Sonication-based environmentally friendly degumming process is very meaningful and important because it can help other research teams try different combinations of degumming process, develop many eco-friendly degumming processes and achieve a wide range of applications.

In order to make cost and technical comparison with conventional degumming process, advantages and limitations of art of environment-friendly silk degumming are listed in **Table 1**. Although conventional soap, alkali or soap-alkali degumming displays their advantages of simple process and wide application, chemicals cannot be recycled, silk fibroin may be damaged, and demand of water and energy is high. For comparison, art of enzyme, CO_2 supercritical fluid, acid, steam and ultrasonic degumming shows different advantages and limitations.

Table 1. Comparison of art of environment-friendly silk degumming with the conventional.

Art	Advantages	Limitations	References
Enzyme	Mild conditions	Relatively high cost	[11][12][13][14][15][16][17][18][19][20][21][22][23][24][25][26][27]
	More choice of enzymes	Easy deactivation	
	Little damage to fibroin High specificity and efficiency		
CO_2 supercritical fluid	Recycling of CO_2	High requirements for equipment	[32][33]
	Little damage to fibroin	Demand of acid pretreatment and ultrasonic post-treatment	
Acid	Smooth and clean surface	Slightly decreased dye uptake percentage	[48][68]

Art	Advantages	Limitations	References
	Increased tensile strength		
Steam	Relative lower cost No addition of chemicals	Lack of industrial application	[57]
Ultrasonic	Improved degumming efficiency Reduced use of water and chemical	Demand of addition of soap, alkali, acid or enzyme Low conversion of electrical to acoustical energy	[38][67][68]
Conventional soap, alkali or soap-alkali [31][73]	Simple process Wide application	Unrecyclable chemicals Damage to fibroin High demand of water and energy [74]	[69][70][71][72] [38][57][67][68]

degumming process, however, Bucciarelli et al. [75] optimized the alkali degumming process with Na_2CO_3 by design of experiment (DOE) and successfully removed all sericin from the silk fibroin with less salt, water, and energy, compared with traditional alkali degumming method, stating that it is possible to make this technique overall more environmentally sustainable. Therefore, traditional degumming process may be developed to become environmentally friendly technique by well-designed experiments.

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