

# Investigation of the effects of environmentally friendly degumming methods on silk dyeing performance

Pervin Anis<sup>1</sup>, Tuba Toprak<sup>1</sup>, Eyuphan Yener<sup>1</sup>  
and Goksen Capar<sup>2</sup>

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## Abstract

In this paper, firstly the effects of environmentally friendly degumming methods on the morphology and structure of fibers have been investigated. Then the dyeing behaviors of environmentally friendly degummed silk fibers were analyzed. In the dyeing process, acid and reactive dyes were used at various dye concentrations. To analyze dyeing characteristics of these fibers, investigations of washing fastness and measurements of color parameters were carried out. Scanning electron microscopy (SEM) images of degummed silk fibers showed that the high temperature (HT) degumming method was more successful than the other methods, but the results were comparable. Weight loss values were also supported by SEM images. Scanning electron microscopy with energy-dispersive X-ray analysis of degummed fibers showed that particles remaining on the surface were the most likely to indicate sericin residue. Fourier transform infrared spectra of raw and degummed fibers with different methods demonstrated typical absorption bands appointed to the peptide bonds (-CONH-) and no major differences were observed. When band intensity was examined, the most intense bands belong to the HT degumming process. The differential scanning calorimetry curves of conventionally and alternatively degummed silk fibers showed two endotherms at around 100°C and 320°C because of water loss and  $\beta$ -sheet fibroin decomposition, respectively. The acid and reactive dyeing of the degummed fibers by environmentally degumming methods gave similar color strength and washing fastness values compared with conventionally degummed fibers.

## Keywords

silk, degumming, dyeing, environmentally friendly, eco-friendly, enzyme

The acceleration of industrialization, the ever-increasing population of the world and deterioration of the water resources, the rapid increase in energy costs and environmental problems, and the enormous sanctions of laws related to the environment make it necessary to develop environmentally friendly processes and use fewer chemicals in the textile industry, which is at the forefront of industries that consume a great deal of clean water and energy and generate high strength wastewaters. Along with resource utilization, waste production also shows a rapid increase.<sup>1–3</sup> As a result, the exhaustion of natural resources associated with increasing consumption demands, safety of the environment, and cost reduction demands have made it necessary to use enzyme-based systems in textiles.<sup>4</sup> In this context, the importance of enzyme-based systems, that is, biotechnology, is increasing day by day, such that the global market for industrial enzymes is

expected to increase from nearly US\$4.6 billion in 2014 to US\$6.3 billion in 2021.<sup>5</sup> Biotechnology is the application of living organisms and their components to industrial processes.<sup>6</sup> The use of enzymes is increasing due to its advantages, such as reduced process time and energy input, working at milder conditions, substrate specificity, and eco-friendly properties,<sup>4,7–11</sup> which are promising for a sustainable textile industry. In the

<sup>1</sup>Uludag University, Faculty of Engineering, Department of Textile Engineering, Gorukle Campus, Bursa, Turkey

<sup>2</sup>Ankara University, Water Management Institute, Gumusdere Agriculture Campus, Ankara, Turkey

## Corresponding author:

Pervin Anis, Uludag University, Faculty of Engineering, Department of Textile Engineering, Gorukle Campus, Nilufer, Bursa 16059, Turkey.  
Email: pervin@uludag.edu.tr

meantime, many researches have been carried out on the inclusion of enzymes in textile processes and there have been several enzymatic treatments of textile materials applied at the industrial scale. Examples of enzyme applications in textile processes can be summarized as desizing with amylases,<sup>12</sup> scouring with pectinase,<sup>13</sup> xylanase,<sup>14</sup> and cutinase,<sup>15</sup> bio-polishing, aging, and depilling with cellulase,<sup>16–18</sup> bleaching with glucose-oxidase,<sup>19–21</sup> residual H<sub>2</sub>O<sub>2</sub> decomposition with catalase<sup>22</sup> for cotton fibers, descaling with papain and protease, anti-shrinkaging with disulfide isomerase and transglutaminase, carbonizing with cellulases<sup>23</sup> for wool fibers, and degumming with proteases for silk fibers.<sup>24</sup>

The discovery of silk fiber obtained from silk worms dates back to B.C. 2700. Silk fibers comprise a fibrous protein, fibroin, and another protein, namely sericin, which has a globular and gummy structure. The percentages of these proteins in a fiber are nearly 75% and 25%, respectively. In addition, the silk fiber contains various impurities (wax, pigment, carbohydrate, inorganic salt).<sup>25</sup> Sericin, which binds the fiber filaments together, gives a dull appearance, and hence it has to be removed from the fiber before dyeing.<sup>26–28</sup>

The process known as degumming or boiling off is the removal of sericin from fibroin by the cleavage of peptide bonds via enzymatic or hydrolytic methods. The degumming processes used in practice are traditional degumming with soap and degumming with synthetic detergents and enzymes.<sup>29</sup> Acid degumming is less used due to the fact that alkaline solution is safer for fibroin than acids.<sup>30</sup> Moreover, the effects of acids and bases depend on the treatment conditions and strengths of the acid and alkali solutions. Strong acids dissolve silk fiber when used in concentration, while dilute acids do not harm the fiber under mild conditions. While hot alkaline solutions dissolve the fiber, diluted alkalis cause damage to the fiber when extra-long treatment time is required at the boiling point.<sup>31</sup> After the degumming process, silk fibers gain a shiny look and excellent softness.<sup>32</sup> Due to the good mechanical strength, toughness, thermal and chemical stability, and biodegradability properties of the fibroin protein, silk fiber has features exceeding that of many natural and man-made fibers.<sup>33–36</sup> Silk fiber, a royal symbol, is also known for its good water absorption capacity and dyeing capability.<sup>25,37</sup>

The removal of sericin from the fiber is an essential step in silk processing and it is currently discarded as waste. However, sericin is a valuable protein and can be recovered from the silk effluents.<sup>38–40</sup> Sericin has antibacterial, anti-cancer, moisturizing, and ultraviolet (UV) resistant properties, so it is a valuable raw material for several industries, including cosmetics, textile, food, biomaterials, and biomedicines.<sup>41–48</sup> Therefore, it is of great importance to recover this protein from the

silk effluents. The conventional degumming with soap at alkaline pH generates wastewaters with high organic content and the soap needs to be separated from the protein, requiring additional treatment steps. In order to recover sericin in the most economical way, the number of steps has to be reduced, which means that alternative degumming methods without chemicals can be useful for generating wastewaters with a lower chemical composition.

The silk fibers are dyed with metal, acid, and reactive dyes, broadly speaking. Although the ability to dye protein fibers with reactive dyes was known of prior to the discovery of these dyes, the formation of covalent bonds between reactive dyes and protein fibers was made clear after the reactive dyes were used in the dyeing of cellulose.<sup>37,49,50</sup> The reactive dyes always were used in silk dyeing because of good wet fastness, brilliancy, diversity in hues, and the possibility to dye using exhaust and continuous dyeing methods and different machines in spite of a large amount of auxiliaries needed and a high wastewater volume.<sup>50,51</sup> Attention should be paid to the brightness, reactivity, and storage ability of reactive dyestuffs to be used in silk dyeing because of silk fiber properties. The appearance of silk fibers is dull, so the brilliancy of reactive dye shades is very important. Since silk fibers are damaged in an alkaline medium at high temperature, reactive dyes that work in an acidic medium are needed. Because the amount of dyestuff required for dyeing silk fibers is small, the storage ability of the reactive dye should be good.<sup>50</sup> Acid dyes are characteristic dyestuffs for the dyeing of protein, polyamide fibers, and blends of them. Among the linkage between protein fibers and acid dyes, salt links are formed because of the opposite character of their charges. In addition to ionic bonds, hydrogen bonds and van der Waals forces are formed, too.<sup>29</sup>

In our previous study, two different eco-friendly degumming (enzymatic and high temperature) processes were applied on silk fibers and the results of these processes showed similarity to conventional degumming with soap.<sup>52</sup> Optimization studies for enzymatic and high temperature treatments revealed that degumming for 30 minutes at an enzyme concentration of 8% and degumming for 20 minutes at 110°C provided the best results for enzymatic and high temperature conditions. The results were evaluated for weight loss, whiteness and brightness values, loss of breaking strength, and elongation.

In this paper, unlike in the previous work, morphological and structural changes of silk fibers degummed by environmentally friendly methods, such as enzymatic and high temperature (HT), were investigated via Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM) analyses. It has been

examined whether any of the changes that may arise have any effect on the dyeing behaviors of silk fibers in dyeing made with different dyes (acid and reactive). To analyze the dyeing behavior of silk fibers, investigations of washing fastness and measurements of color parameters were carried out.

## Experimental work

### Materials

The raw silk fibers were obtained from Kirman İplik San. ve Tic. Ltd Şti., Bursa, Turkey. The commercial reactive (Novacron Brilliant Red FN-3GL) and acid (Lanaset Red 2B) dyes, wetting agent (Albaflow Jet), and leveling agent (Albegal) were kindly provided by Huntsman Cooperation, Turkey. For reactive dyeing, the leveling agent (Velsodye BBK) was supplied by Onan Kimya, Turkey. Sodium sulfate, formic acid, and ammonia (25%) were of analytical reagent grade. Savinase 16 L, a protease (Novozymes), which was produced from *Bacillus sp.*, was used in enzymatic degumming processes.

### Methods

**Degumming.** The enzymatic degumming process was carried out with a protease enzyme in a Dyetech Polybath Sample Dyeing Machine with 10 g fibers. The ratio of the volume of liquor to the weight of fabric, amount of enzyme, and duration and temperature of the process were detected after detailed optimization studies<sup>52</sup> and they were chosen as 10:1, 8%, 30 minutes, and 50°C, respectively. The pH values were determined with the highest precision. The pH value of the degumming bath was adjusted by an ammonia and ammonium chloride mixture. At the end of this process, to deactivate the enzyme a rinsing process was performed for 10 minutes at 70°C. Then, a neutralization process using acetic acid (2 g/l) was

performed at the same temperature. The fibers were washed in tap water and then dried in the open air.

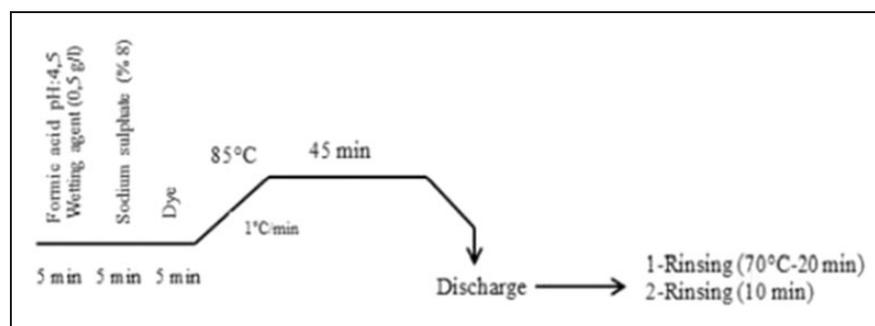
The high temperature (HT) degumming treatment was done in an ATAC Sample Dyeing Machine (high temperature–high pressure sample dyeing machine) with 10 g fibers. The parameters of HT treatment were determined according to optimization studies.<sup>52</sup> The duration and liquor ratio were 20 minutes and 1:18, respectively. For the HT degumming procedure, treatment started at 30°C and then increased to 110°C with a rate of 2°C/min. The silk fibers were treated at this temperature for 20 minutes. After that, fibers were rinsed with hot water (70°C) for 10 minutes twice and washed in tap water, respectively. The degummed fibers were dried in the open air.

To compare the efficiency of the environmentally friendly degumming methods, the conventional method with soap was also carried out in the Dyetech Polybath Sample Dyeing Machine with 10 g fibers. This process was done for 45 minutes at 98°C with soap (3.30 g/l), Na<sub>2</sub>CO<sub>3</sub> (2.26 g/l), Albegal (0.2 ml/l), and a water containing bath. The liquor ratio and pH values were 27:1 and 9.5, respectively. The fibers were rinsed twice with water at 70°C and then subjected to neutralization.

**Dyeing.** All the dyeing processes were carried out in the Dyetech Polybath Sample Dyeing Machine at 1:20 liquor ratio with 10 g silk fibers. The pH values of the dyebath were adjusted to 4.5 with formic acid. The dye concentrations were chosen as 1, 2, 5% owf (on the weight of the fabric) from light to dark shades, respectively. The acid and reactive dyeing diagrams are presented in Figures 1 and 2, respectively.

The results of dyeing and degumming treatments were analyzed using the following methods.

**Color characteristics.** Using the ColorMission v.3.4.1 by Argetek program with a Konica Minolta CM-3600A spectrophotometer (illuminant D65; 10° standard



**Figure 1.** Acid dyeing process.

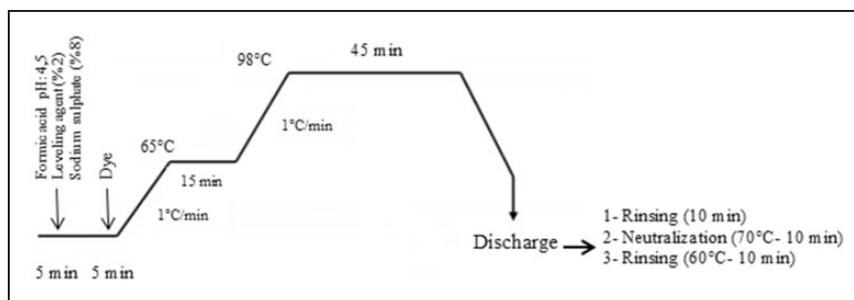


Figure 2. Reactive dyeing process.

observer), based on reflectance measurements, the  $L^*$ ,  $a^*$ ,  $b^*$  coordinate values were obtained. The color strength ( $K/S$ ) and color differences ( $\Delta E^*$ ) formulas are presented in Equations (1) and (2), respectively. The  $K/S$  value was calculated using the Kubelka–Munk equation (1). The  $K/S$  value was calculated for the wavelength corresponding to the maximum absorption value (510 and 520 nm). The  $\Delta E^*$  value was calculated according to the CIELAB 1976 equation (2)

$$K/S = \frac{(1 - R)^2}{2R} \quad (1)$$

In the Equation (1),  $R$  is the decimal fraction of the reflectance of fabric,  $K$  is the absorption coefficient, and  $S$  is the scattering coefficient<sup>53</sup>

$$\Delta E_{CIELAB}^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (2)$$

**Washing fastness.** The washing fastness of the dyed fibers was carried out by a TEST color fastness tester, using the color fastness to domestic and commercial laundering standard test method (TS EN ISO 105-C06/A1S).

**Fiber surface analysis.** The surface morphologies of the treated silk fibers were examined by means of SEM, using a Tescan Vega3 SBU. Samples were observed at 15 keV acceleration voltages, after gold coating under reduced argon atmosphere with a Cressington Sputter Coater-108auto. Quantitative elemental analysis (energy-dispersive X-ray spectroscopy (EDX)) was also performed for a single fiber with the Tescan Vega3 SBU by means of a module.

**Thermal analysis.** The DSC analyses were performed by a PerkinElmer Instruments Sapphire Differential Scanning

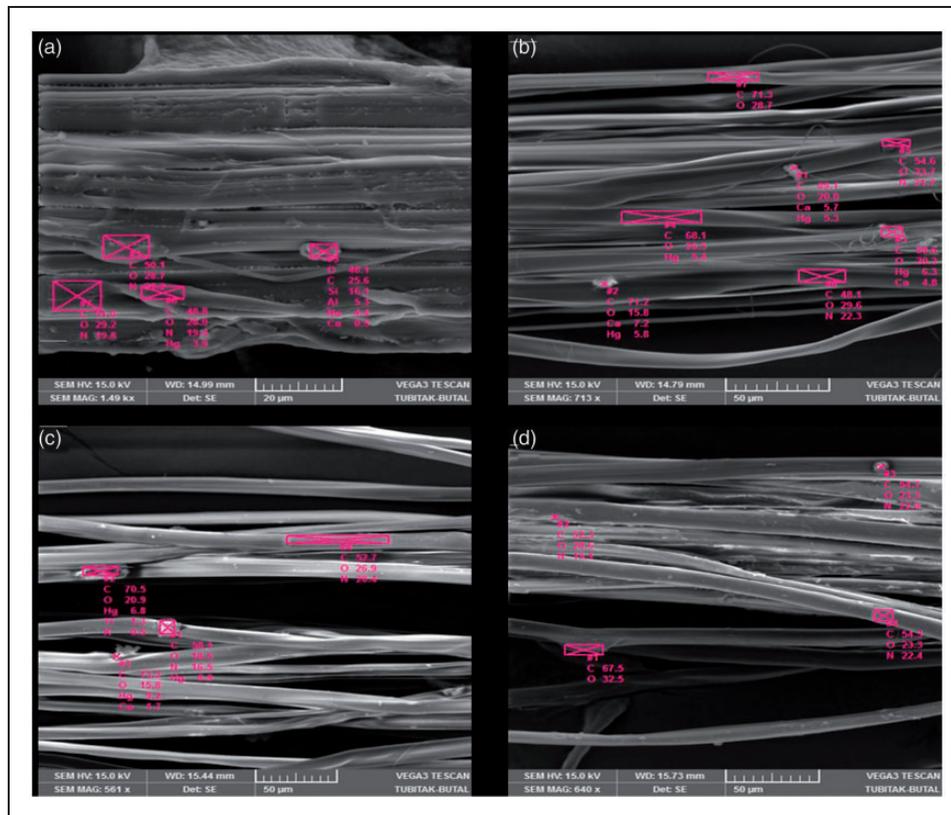
Calorimeter. Samples of about 1–2 mg of fibers were sealed in standard aluminum pans and submitted to DSC analysis from 20°C to 350°C, at a heating rate of 10–20°C/min, under the flux of nitrogen.

**FTIR analysis.** FTIR spectra of the samples were obtained using a Jasco FT/IR-4700 infrared spectrometer by the attenuated total reflection (ATR) method. This device measures in the region of 350–7800  $\text{cm}^{-1}$  at room temperature. Spectra were acquired at 4  $\text{cm}^{-1}$  resolution.

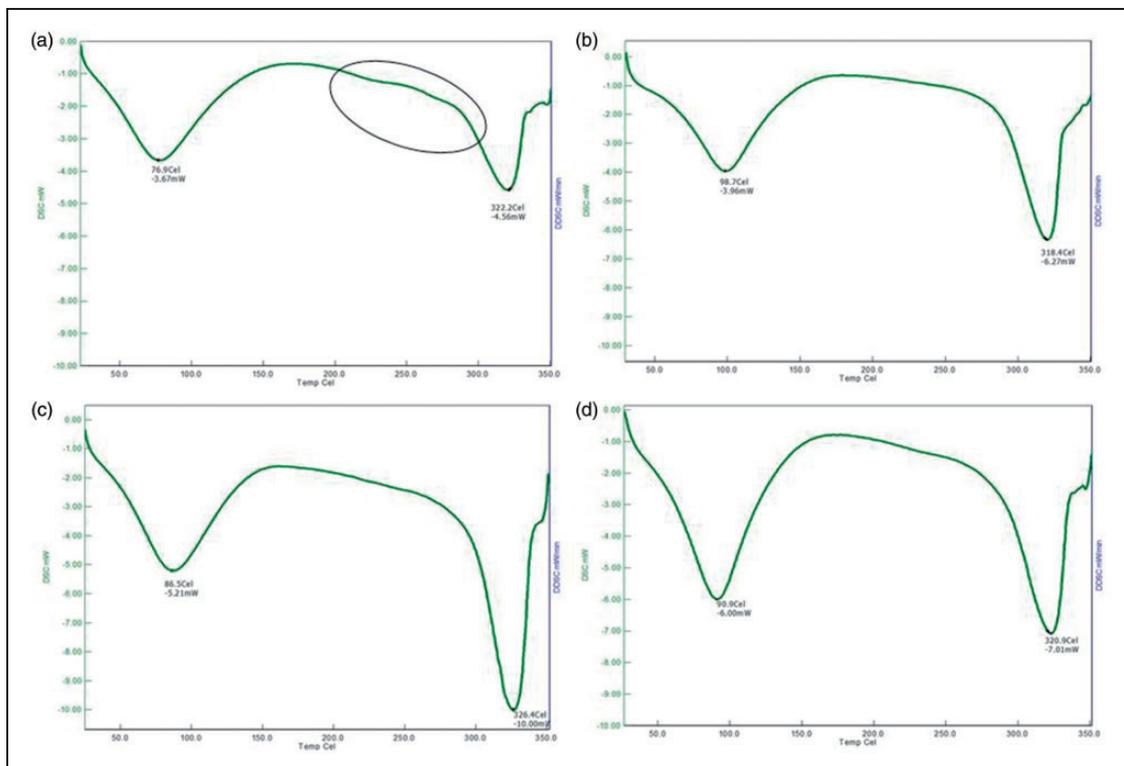
## Results and discussion

### Morphological characterization

Surface morphology changes of the silk fibers after different degumming processes were investigated using SEM. The SEM micrographs of raw, conventional, HT, and enzymatic treated fibers are presented in Figure 3. All of the treated SEM micrographs showed the presence of sericin residues on the surface of the silk yarns. As shown in Figure 3, the EDX analysis was carried out to determine whether the surface particles were residues of the sericin. It was seen that the components of these residues were C, O, N. This most likely indicated sericin residue. Both of the morphological analyses showed that environmental degumming procedures removed only sericin. These images also showed that smoother surfaces were obtained without interfering with the fibroin part of the fiber, that is, no fiber degradation occur during degumming. The HT degummed silk sample (Figure 3(c)) showed a cleaner and smoother surface than the conventional and enzymatic degummed fibers, respectively. There was conformity between the SEM images of the samples degummed by various methods and weight loss of fibers. If the weight losses in the degumming process were ordered from large to small, this sequence was HT (22.7%), conventional (20.6%), and enzymatic degumming (19.4%).<sup>52</sup>



**Figure 3.** Scanning electron microscopy images of raw (a) and degummed silk fibers with various methods: (b) conventional degumming; (c) high temperature degumming; (d) enzymatic degumming.



**Figure 4.** Differential scanning calorimetry (DSC) analysis of raw (a) and degummed silk fibers with various methods: (b) conventional degumming; (c) high temperature degumming; (d) enzymatic degumming.

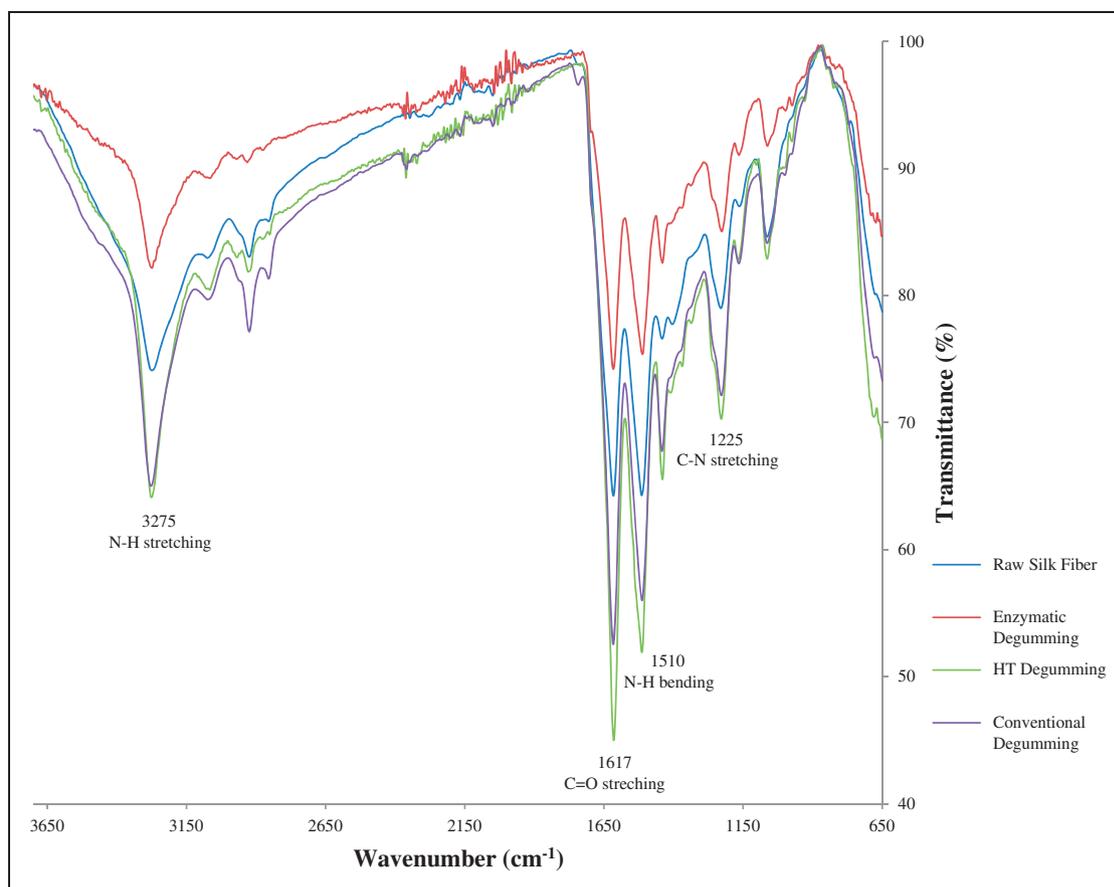
### DSC analysis

Figure 4 presents standard DSC curves for the raw and degummed silk fibers. All curves in Figure 4 show two prominent endothermic peaks. One of them is at low temperatures due to the loss of water, while another is at high temperatures associated with degradation phenomena, which can be considered as thermal signatures of protein carbonization.<sup>54,55</sup> With the raw silk sample, an endothermic peak was observed at around 320°C, which was attributed to the thermal degradation of material  $\beta$ -sheet form.<sup>56–59</sup> When the curves of the other samples (curves b, c, d) were examined, it was seen that their endothermic peaks at around 320°C were very close to that of the raw silk fibers.<sup>60</sup> This could be because the degumming processes did not cause significant structural changes in the fibers. In the curve of raw silk fiber at around 225–275°C, two very slight peaks were seen in the circle. Their presence might be explained by non-isothermal crystallization before degradation<sup>61</sup> due to the presence of an

amorphous sericin. The additional thermal energy of DSC might have induced a significant  $\beta$ -sheet increment during scanning.<sup>61</sup>

### Spectroscopic characterization

Changes in the structure of silk fibers treated with various degumming treatments were determined by FTIR-ATR and they are presented in Figure 5. According to Gupta et al.,<sup>62</sup> proteins have characteristic energy absorption wavenumbers, such as 1650–1630  $\text{cm}^{-1}$  for primary amides, 1540–1520  $\text{cm}^{-1}$  for secondary amides, and 1270–1230  $\text{cm}^{-1}$  for tertiary amides. The vibrational absorption of the phenol groups in the tyrosine are defined by the signal at 1160  $\text{cm}^{-1}$ .<sup>63</sup> In addition, the positions of these peaks confirmed the protein, such as 1650  $\text{cm}^{-1}$  (random coil) and 1630  $\text{cm}^{-1}$  ( $\beta$ -sheet) for amide I, 1540  $\text{cm}^{-1}$  (random coil) and 1520  $\text{cm}^{-1}$  ( $\beta$ -sheet) for amide II, and 1230  $\text{cm}^{-1}$  (random coil) and 1260  $\text{cm}^{-1}$  ( $\beta$ -sheet) for amide III.<sup>62,64,65</sup> Moreover, in the literature there



**Figure 5.** Fourier transform infrared spectra of degummed silk fibers with various methods (undyed). HT: high temperature.

is information that sericin gives peaks at 3200, 1600, and 1500  $\text{cm}^{-1}$  wavelengths, which are wider than those of fibroin.<sup>66–70</sup> From inspection of the transmittance spectra depicted in Figure 5, the broad spectrum from 3600 to 3100  $\text{cm}^{-1}$  and the peak at around 3275  $\text{cm}^{-1}$  are representative of the N–H stretching band that is built on the O–H stretching band in the silk. The peak at around 1610  $\text{cm}^{-1}$  probably represents C=O stretching (amide I), while the secondary amides at approximately 1510  $\text{cm}^{-1}$  (N-H bending) and the tertiary amides in the region of 1225  $\text{cm}^{-1}$  are due to the stretch of the bond C–N.<sup>66,71–77</sup> According to Figure 5, no major difference was observed in the IR spectra of the degummed silk fibers.

On the basis of the intensity of the amide bands, the most intense bands belong to the HT degumming process, so the most amount of sericin was removed by this process and, because the ATR technique was used, the amount of fibroin included in the measurement increased as the amount of sericin was removed. The conventional process gave close results to the HT process, but enzymatic degumming

signals were only slightly less than both of them. These results were in compliance with weight loss values; namely, the HT degumming process had the greatest weight loss and the highest band intensity, while the enzymatic degumming process had the lowest weight loss and band intensity among the degumming processes.

### Evaluation of color strength and fastness properties

The acid and reactive dyed samples showed the maximum absorption wavelength at 510 and 520 nm, respectively. The color values of dyed samples are presented in Table 1.

According to Table 1, it can be concluded that the *K/S* values of the dyed samples after alternative degumming processes (enzymatic and HT) were approximately the same as those of the samples subjected to the dyeing after degumming by the conventional method. The *K/S* value of dyed material is closely related to the amount of dye absorbed. In this study, it was obvious that the *K/S* value increased as

**Table 1.** Color values of dyed samples

Degumming process	<i>L</i> *	<i>a</i> *	<i>b</i> *	<i>K/S</i>	$\Delta E^*$	
1% acid dyeing						
Enzymatic	59.0353	45.2966	11.0010	3.32	1.178	
Conventional	59.2147	46.3179	11.5604	3.42		2.069
HT	60.0394	44.4408	11.2812	3.07		
1% reactive dyeing						
Enzymatic	55.6886	53.5584	18.1052	6.17	0.95	
Conventional	55.3084	53.9377	18.8885	6.47		1.521
HT	53.8275	53.5961	18.9358	7.30		
2% Acid Dyeing						
Enzymatic	48.9869	53.4945	18.0607	10.10	1.417	
Conventional	50.2056	52.8667	17.7006	8.79		0.251
HT	50.0341	52.6830	17.6997	9.06		
2% reactive dyeing						
Enzymatic	49.4884	57.2206	24.7622	12.71	0.795	
Conventional	49.9506	57.8597	24.6611	12.90		2.158
HT	50.1949	56.3302	23.1585	11.42		
5% acid dyeing						
Enzymatic	40.0423	55.0410	26.7690	23.64	1.690	
Conventional	41.4272	55.8078	26.1775	23.52		1.965
HT	40.7034	54.4881	24.9148	23.40		
5% reactive dyeing						
Enzymatic	44.1435	58.8513	31.0768	22.93	1.863	
Conventional	44.6273	59.9308	32.5157	22.70		1.551
HT	43.5931	59.0056	31.8229	25.05		

HT: high temperature.

the dye concentration increased. This increment was more pronounced for acid dye for all dyestuff concentrations.

In the evaluations of color differences ( $\Delta E^*$ ), the samples subjected to traditional degumming and subsequently dyeing were accepted as standard and  $\Delta E^*$  values for acid and reactive dyes in each dyestuff concentration were found to be around 2. The color difference values were prominent in acid and reactive dyeing at 2% concentration. Therefore, these samples were also subjected to visual analysis with 23 observers. The observers had normal color vision according to

the Ishihara test and few of them were experienced in the assessment of color differences. A total of 552 visual assessments were made under the D65 (daylight) illuminant. According to the visual analysis, for acid dyeing, 78% of observers monitored no color difference between conventional and HT degumming, while 95% of them observed color difference between conventional and enzymatic degumming. However, for the visual evaluation of reactive dyed samples, 100% and 52% of viewers observed color differences between conventional-HT and conventional-enzymatic degumming, respectively.

**Table 2.** Washing fastness values of acid dyed samples

Degumming processes	Washing fastness values						
	Fading values	Wool	Acrylic	Polyester	Nylon	Cotton	Acetate
5% acid dyeing							
Conventional	3–4	3–4	3–4	4	1	4	3–4
Enzymatic	4	3–4	4–5	4	2	3–4	4–5
HT	4	4–5	4–5	4–5	1–2	3–4	4–5
2% acid dyeing							
Conventional	4	4–5	4	4–5	2	4–5	4–5
Enzymatic	4	4	4–5	4–5	2–3	4	5
HT	4	4–5	4–5	4–5	2–3	4–5	5
1% acid dyeing							
Conventional	4–5	4	4	4–5	2	4–5	5
Enzymatic	4	4	4–5	4–5	2–3	4–5	5
HT	4–5	5	4–5	4–5	3	4–5	4–5

HT: high temperature.

**Table 3.** Washing fastness values of reactive dyed samples

Degumming processes	Washing fastness values						
	Fading values	Wool	Acrylic	Polyester	Nylon	Cotton	Acetate
5% reactive dyeing							
Conventional	4	4	4	3–4	4	3	4
Enzymatic	4	4	4–5	4–5	4–5	4	4–5
HT	4–5	4	4–5	4	4	4	4
2% reactive dyeing							
Conventional	4–5	4–5	4–5	4	4	4–5	5
Enzymatic	4–5	4–5	4–5	4	4–5	4	4–5
HT	4–5	4–5	4–5	4–5	4–5	4–5	5
1% reactive dyeing							
Conventional	4–5	5	4–5	4–5	4–5	4–5	5
Enzymatic	4–5	4	4–5	4–5	4	5	4–5
HT	4–5	5	4–5	4–5	3	4–5	4–5

HT: high temperature.

The fastness ratings of silk fibers dyed at 1%, 2%, and 5% (owf) dye concentrations are presented in Tables 2 and 3. The same values were obtained for the samples degummed by alternative procedures in comparison to the samples degummed by the conventional method after acid and reactive dyeing. The staining rates were good to very good (4 to 4–5). In general, with the reactive dyes, better fastness values of about half a point were received compared to acid dyes because of covalent bonds. As expected, the increase in dyestuff concentration caused the fading values to fall by about half a point. The only exception was the detection of nylon fiber, which is due to the nylon dyeing of the acid dye.

## Conclusion

The results of this research could be summarized as follows.

The HT and enzymatic degumming processes removed sericin from the silk fibers, which was confirmed by SEM, FTIR, and DSC analyses. According to the SEM images and weight losses, the HT degumming process removed more sericin than the other methods. Enzymatic and conventional processes also provided sufficient cleaning by removing sericin in high amounts. FTIR analysis for the degummed samples and raw silk showed similar peaks. The degumming processes increased the number of groups, such as NH, C=O, C–N, and the HT degumming had the most intense bands because of the removed sericin. FTIR results also overlapped weight loss values. Furthermore, the EDX analysis confirmed that the surface particles were likely to be sericin residues due to the C, O, and N components of these residues. The DSC curves of eco-friendly and conventional degummed silk fibers showed two endotherms corresponding to water loss and  $\beta$ -sheet fibroin decomposition at around 100°C and 320°C, respectively. The closed peaks that were interpreted as degumming processes did not cause significant changes in the fibers. When the effects of environmental degumming applications on the dyeing processes carried out at different concentrations of acid and reactive dyes were examined on the basis of  $K/S$ ,  $\Delta E^*$ , and washing fastness values, it was found that these values were close to those of conventionally treated samples. Although there was no significant difference between the acid and reactive dyestuffs in the washing fastness values, the values after the reactive dyeing were about half a point better.

As a result, the HT and enzymatic degumming methods, which were more environmentally friendly than the conventional method, eliminate the use of chemicals in the degumming process and had no negative effects on the dyeing behavior of the silk fibers, so the alternative methods represent hope for the textile industry.

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## References

1. Chatha SAS, Asgher M and Iqbal HMN. Enzyme-based solutions for textile processing and dye contaminant biodegradation—a review. *Environ Sci Pollut Res* 2017; 24: 14005–14018.
2. Singh R, Kumar M, Mittal A, et al. Microbial enzymes: industrial progress in 21st century. *3 Biotech* 2016; 6: 1–15.
3. Varadarajan G and Venkatachalam P. Sustainable textile dyeing processes. *Environ Chem Lett* 2016; 14: 113–122.
4. Choi JM, Han SS and Kim HS. Industrial applications of enzyme biocatalysis: current status and future aspects. *Biotechnol Adv* 2015; 33: 1443–1454.
5. Dewan SS. *Global Markets for Enzymes in Industrial Applications*. Report, Business Communications Company Inc, USA, January 2017.
6. Alat DV. Recent developments in the processing of textiles using enzymes. *Colourage* 2001; 48: 33–36.
7. Carlier F. Enzymes. *Ind Textila* 2001; 54: 121–123.
8. Ethers JN and Anis PA. Textile enzyme use: a developing technology. *Am Dyest Report* 1998; 77: 18–23.
9. Naik SR and Paul R. Application of enzymes in textile processing. *Asian Text J* 1997; 6: 48–55.
10. Warke VV and Chandratre PR. Application of biotechnology in textiles. *Man-made Text India* 2003; 26: 142–146.
11. Li S, Yang X, Yang S, et al. Technology prospecting on enzymes: application, marketing and engineering. *Comput Struct Biotechnol J* 2012; 2: e201209017.
12. Chand N, Nateri AS, Sajedi RH, et al. Enzymatic desizing of cotton fabric using a Ca<sup>2+</sup>-independent  $\alpha$ -amylase with acidic pH profile. *J Mol Catal B Enzym* 2012; 83: 46–50.
13. Stănescu MD, Dochia M, Fogoraşi M, et al. Enzymes in cotton bio- scouring. *U P B Sci Bull Ser B* 2010; 72: 21–28.

14. Csiszár E, Losonczy A, Koczka B, et al. Degradation of lignin-containing materials by xylanase in biopreparation of cotton. *Biotechnol Lett* 2006; 28: 749–753.
15. Yan H, Hua Z, Qian G, et al. Effect of cutinase on the degradation of cotton seed coat in bio-scouring. *Biotechnol Bioprocess Eng* 2009; 14: 354–360.
16. Cortez J, Ellis J and Bishop D. Cellulase finishing of woven, cotton fabrics in jet and winch machines. *J Biotechnol* 2001; 89: 239–245.
17. Esfandiari A, Firouzi-Pouyaei E and Aghaei-Meibodi P. Effect of enzymatic and mechanical treatment on combined desizing and bio-polishing of cotton fabrics. *J Text Inst* 2014; 105: 1193–1202.
18. Saravanan D, Vasanthi NS and Ramachandran T. A review on influential behaviour of biopolishing on dyeability and certain physico-mechanical properties of cotton fabrics. *Carbohydr Polym* 2009; 76: 1–7.
19. Tzanov T, Costa SA, Gübitz GM, et al. Hydrogen peroxide generation with immobilized glucose oxidase for textile bleaching. *J Biotechnol* 2002; 93: 87–94.
20. Eren H, Anis P and Davulcu A. Enzymatic one-bath desizing—bleaching—dyeing process for cotton fabrics. *Text Res J* 2009; 79: 1091–1098.
21. Bankar SB, Bule MV, Singhal RS, et al. Glucose oxidase—an overview. *Biotechnol Adv* 2009; 27: 489–501.
22. Amorim AM, Gasques MDG, Andreus J, et al. The application of catalase for the elimination of hydrogen peroxide residues after bleaching of cotton fabrics. *An Acad Bras Cienc* 2002; 74: 433–436.
23. Cavaco-Paulo A. Processing textile fibers with enzymes: an overview. In: Eriksson KEL and Cavaco-Paulo A (eds) *ACS Symposium Series*. Washington DC: American Chemical Society, 1998, pp. 180–189.
24. Cavaco-Paulo A and Gubitz G. Catalysis and processing. In: Cavaco-Paulo A and Gubitz G (eds) *Textile Processing with Enzymes*. Cambridge: Woodhead Publishing Limited, 2003, pp. 87–119.
25. Hosseini M, Montazer M and Damerchely R. Enhancing dye-ability and antibacterial features of silk through pre-treatment with chitosan. *J Eng Fiber Fabr* 2013; 8: 164–167.
26. Kaplan D, Adams WW, Farmer B, et al. Silk: biology, structure, properties, and genetics. In: Kaplan D, Adams W, Farmer B, et al. (eds) *Silk Polymers*. Washington DC: American Chemical Society, 1994, pp. 2–16.
27. Shimizu M. Structural basis of silk fibre. In: Hojo N (ed.) *Structure of Silk Yarn: Biological and Physical Aspects Pt. A*. Enfield: Taylor & Francis Inc., 2000, pp. 7–17.
28. Sheikh MRK, Farouqui FI, Modak PR, et al. Dyeing of Rajshahi silk with basic dyes: effect of modification on dyeing properties. *J Text Inst* 2006; 97: 295–300.
29. Chattopadhyay D.P. Chemistry of dyeing. In: Clark M (ed.) *Handbook of Textile and Industrial Dyeing Volume 1: Principles, Processes and Types of Dyes*. Cambridge: Woodhead Publishing Limited, 2011, pp. 64–147.
30. Ngoka BM, Nguku EK, Kioko EN, et al. Extraction of natural silk fibre from cocoons of argema mimosae (Lepidoptera: Saturniidae). *J Agric Sci Technol A* 2015; 5: 846–853.
31. Rehman R, Mahmud S, Habib MA, et al. A revolution of silk dyeing with FL based cotton-reactive dyes. *Int J Text Sci* 2015; 4: 42–52.
32. Tao H, Amsden JJ, Strikwerda AC, et al. Metamaterial silk composites at terahertz frequencies. *Adv Mater* 2010; 22: 3527–3531.
33. Vollrath F and Porter D. Silks as ancient models for modern polymers. *Polymer* 2009; 50: 5623–5632.
34. Vepari C and Kaplan DL. Silk as a biomaterial. *Progr Polym Sci (Oxford)* 2007; 32: 991–1007.
35. Lu Q, Zhu H, Zhang C, et al. Silk self-assembly mechanisms and control from thermodynamics to kinetics. *Biomacromolecules* 2012; 13: 826–832.
36. Cai Z, Jiang G and Qiu Y. Chemical modification of Bombyx mori silk with epoxide EPSIB. *J Appl Polym Sci* 2004; 91: 3579–3586.
37. Koushic U and Hossain S. A comparative study on silk dyeing with acid dye and reactive dye. *Int J Eng Technol* 2010; 10: 22–27.
38. Capar G, Aygun SS and Gecit MR. Treatment of silk production wastewaters by membrane processes for sericin recovery. *J Memb Sci* 2008; 325: 920–931.
39. Capar G, Aygun SS and Gecit MR. Separation of sericin from fatty acids towards its recovery from silk degumming wastewaters. *J Memb Sci* 2009; 342: 179–189.
40. Capar G. Separation of silkworm proteins in cocoon cooking wastewaters via nanofiltration: effect of solution pH on enrichment of sericin. *J Memb Sci* 2012; 389: 509–521.
41. Mondal M, Trivedy K and Kumar SN. The silk protein, sericin and fibroin in silkworm, Bombyx mori Linn.-a review. *Casp J Env Sci* 2007; 5: 63–76.
42. Ting-Ting Cao Y-QZ. Processing and characterization of silk sericin from Bombyx mori and its application in biomaterials and biomedicines. *Mater Sci Eng C* 2016; 61: 940–952.
43. Gupta D, Chaudhary H and Gupta C. Sericin-based polyester textile for medical applications. *J Text Inst* 2015; 106: 366–376.
44. Fatahian R, Noori M, Khajavi R, et al. Exrtaction of sericin from degumming process of silk fibres and its application on nonwoven fabrics. *Int J Adv Chem* 2017; 5: 25–28.
45. Zhang Y-Q. Application of natural silk sericin protein in biomaterials. *Biotechnol Adv* 2002; 20: 91–100.
46. Rajendran R, Balakumar C, Sivakumar R, et al. Extraction and application of natural silk protein sericin from Bombyx mori as antimicrobial finish for cotton fabrics. *J Text Inst* 2012; 103: 458–462.
47. Aramwit P, Siritientong T and Srichana T. Potential applications of silk sericin, a natural protein from textile industry by-products. *Waste Manag Res* 2012; 30: 217–224.
48. Padamwar MN, Pawar AP, Daithankar AV, et al. Silk sericin as a moisturizer: an in vivo study. *J Cosmet Dermatol* 2005; 4: 250–257.
49. Gulrajani ML. Dyeing of silk with reactive dyes. *Rev Prog Color Relat Top* 1993; 23: 51–56.
50. Zuwang W. Recent developments of reactive dyes and reactive dyeing of silk. *Rev Prog Color Relat Top* 1998; 28: 32–38.

51. Agarwal D, Sen K and Gulrajani ML. Dyeing of silk with bifunctional reactive dyes: the relationship between exhaustion and fixation. *J Soc Dye Colour* 1997; 113: 174–178.
52. Anis P, Capar G, Toprak T, et al. Sericin removal from silk fibers with eco-friendly alternative methods. *Tekst ve Konfeksiyon* 2016; 26: 368–374.
53. Nagia FA and EL-Mohamedy RSR. Dyeing of wool with natural anthraquinone dyes from *Fusarium oxysporum*. *Dye Pigment* 2007; 75: 550–555.
54. Magoshi J and Nakamura S. Studies on physical properties and structure of silk. Glass transition and crystallization of silk fibroin. *J Appl Polym Sci* 1975; 19: 1013–1015.
55. Rocha LKH, Favaro LIL, Rios AC, et al. Sericin from *Bombyx mori* cocoons. Part I: extraction and physico-chemical-biological characterization for biopharmaceutical applications. *Process Biochem* 2017; 61: 163–177.
56. Tsukada M, Freddi G, Gotoh Y, et al. Physical and chemical properties of tussah silk fibroin films. *J Polym Sci Part B Polym Phys* 1994; 32: 1407–1412.
57. Tsukada M. Effect of the drying rate on the structure of TusSah silk (*Antheraea pernyi*) fibroin. *J Polym Sci Polym Phys* 1986; 24: 457–460.
58. Kweon HY, Um IC and Park YH. Thermal behavior of regenerated *Antheraea pernyi* silk fibroin film treated with aqueous methanol. *Polymer (Guildf)* 2000; 41: 7361–7367.
59. Liu L, Yang X, Yu H, et al. Biomimicking the structure of silk fibers via cellulose nanocrystal as  $\beta$ -sheet crystallite. *RSC Adv* 2014; 4: 14304–14313.
60. Freddi G, Monti P, Nagura M, et al. Structure and molecular conformation of Tussah silk fibroin films: effect of heat treatment. *J Polym Sci B Polym Phys* 1996; 35: 841–847.
61. Hu X, Shmelev K, Sun L, et al. Regulation of silk material structure by temperature-controlled water vapor annealing. *Biomacromolecules* 2011; 12: 1686–1696.
62. Gupta D, Agrawal A and Rangi A. Extraction and characterization of silk sericin. *Indian J Fibre Text Res* 2014; 39: 364–372.
63. Shao J, Zheng J, Liu J, et al. Fourier transform Raman and Fourier transform infrared spectroscopy studies of silk fibroin. *J Appl Polym Sci* 2005; 96: 1999–2004.
64. Vasconcelos Costa AJ. *Protein matrices for wound dressings*. PhD Thesis, Universidade do Minho Escola de Engenharia, Portugal, 2010.
65. Wojciechowska E, Włochowicz A and Weselucha-Birczyńska A. Application of Fourier-transform infrared and Raman spectroscopy to study degradation of the wool fiber keratin. *J Mol Struct* 1999; 511–512: 307–318.
66. Doakhan S, Montazer M, Rashidi A, et al. Influence of sericin/TiO<sub>2</sub> nanocomposite on cotton fabric: Part 1. Enhanced antibacterial effect. *Carbohydr Polym* 2013; 94: 737–748.
67. Gupta D, Agrawal A, Chaudhary H, et al. Cleaner process for extraction of sericin using infrared. *J Clean Prod* 2013; 52: 488–494.
68. Yang Y, Lee SM, Lee HS, et al. Recovery of silk sericin from soap-alkaline degumming solution. *Int J Ind Entomol* 2013; 27: 203–208.
69. Srihanam P. Silk fibroin/starch blend films: preparation and characterization. *Biotechnology* 2011; 10: 114–118.
70. Dhandayuthapani B, Yasuhiko Y, Maekawa T, et al. Fabrication and characterization of nanofibrous scaffold developed by electrospinning. *Mater Res* 2011; 14: 317–325.
71. Hu X, Kaplan D and Cebe P. Determining beta-sheet crystallinity in fibrous proteins by thermal analysis and infrared spectroscopy. *Macromolecules* 2006; 39: 6161–6170.
72. Freddi G, Tsukada M and Beretta S. Structure and physical properties of silk fibroin/polyacrylamide blend films. *J Appl Polym Sci* 1998; 71: 1563–1571.
73. Freddi G, Pessina G and Tsukada M. Swelling and dissolution of silk fibroin (*Bombyx mori*) in N-methyl morpholine N-oxide. *Int J Biol Macromol* 1999; 24: 251–263.
74. Lu Q, Hu X, Wang X, et al. Water-insoluble silk films with silk I structure. *Acta Biomater* 2010; 6: 1380–1387.
75. de Moraes MA, Nogueira GM, Weska RF, et al. Preparation and characterization of insoluble silk fibroin/chitosan blend films. *Polymers (Basel)* 2010; 2: 719–727.
76. Mingzhong L, Kuga S and Nishiyama Y. Controlling molecular conformation of regenerated wild silk fibroin by aqueous ethanol treatment. *Polym Adv Technol* 2003; 14: 694–698.
77. Fabian H and Mantele W. Infrared spectroscopy of proteins. In: Chalmers JM and Griffiths PR (eds) *Handbook of Vibrational Spectroscopy Volume 5: Applications in Life, Pharmaceutical and Natural Sciences*. Chichester: John Wiley & Sons Ltd., 2002, pp. 3749–3775.