The protective ability of Camellia meal extract on the silk protein

JZ Weng1,*, C Cai, DY Zhang, BK Dai

1 College of Chemistry and Material Science, Fujian Normal University Fuzhou
*E-mail: jackyweng@vip.163.com

Abstract. With the enhancement of living standards, people pay more and more attention to the health. The edible oil become more and more popular, but also produced a large amount of Camellia meal which can not fully put into utilization. In this study, the extracting liquid of Camellia meal was used on the process of silk degumming. Firstly, tussah silk was treated by degumming in the Na2CO3 solution, and the preliminary condition of tussah silk degumming was obtained by orthogonal experiment: the concentration Na2CO3 was 0.1%, the degumming time was 1 hour, and the ratio of silk/water was 40:1. Then the extract of Camellia meal (GCJSY) was added before the bleaching process of tussah silk to investigate the protective ability of GCJSY on the silk protein basry on the residual ratio of the silk. While the concentration of GYJSY was 0.08%, the residual ratio of silk after degumming in the Na2CO3 solution and bleaching in the 2% H2O2 solution was 87.2%.

1. Preface
China is the hometown of silk. Silk is a kind of natural macromolecule material with good mechanical properties[1]. Silk is mainly composed of the inner silk fibroin and the outer layer sericin[2]. Silk sericin, which is composed of 18 kinds of amino acids, plays a protective and adhesive role in silk fibroin, which is mainly composed of globular proteins. Sericin accounted for 20%~30% in the silkworm silk, and accounted for about 12%~13% in tussah silk[3]. Recent studies shown that sericin has great potential application in functional materials[4]. Therefore, the selection of suitable additives could help to form sericin protein composite[5], which also will help to maintain the quality of silk and will expand the functional materials applications based on the silk protein composite[6]. In recent years, great efforts have been made to develop Camellia meal plantation in China.

With the production of tea oil, a large amount of Camellia meal producing residue--Camellia meal has been produced[7]. At present, the application of Camellia meal in our country was still not enough, most of the detoxification simple as feed or directly as cleaning agent, fuel, fertilizer use[8]. So the Camellia meal was resulting in a serious waste of resources. The main components of Camellia meal were some natural organic polymer, such as tea saponin, cellulose, protein and polysaccharide, which
can be exacted by biomass refining technology and their equitable applications were the current research focus[9].

In this paper, tussah silk was firstly treated by degumming in the Na2CO3 solution, and the preliminary condition of tussah silk degumming was obtained by orthogonal experiment. Then, the protective ability of the extracted liquid of the Camellia meal on the silk protein were studied.

2. Experimental

2.1 Main reagents
All reagents were used as received without further purification. Camellia meal were provided by factory. Tussah cocoon, modifier and catalyst were provided by research group. HCl(AR) was purchased from Quanzhou Donghai Reagent Co., Ltd. NaOH(AR) was purchased from Sinopharm Chemical Reagent Co. Ltd. H2O2 was purchased from Sinopharm Chemical Reagent Co., Ltd, Na2CO3 was purchased from Guangdong Chemical Reagent Engineering Technology Research and Development Center.

2.2 Experiment content
2.2.1 Preparation of GCJSY
A certain amount of Camellia meal was added into the three necked flask, then water, modifiers, and catalysts were also added. The reacting temperature was controlled at 60°C, and the solution was magnetically stirred with a constant rotation rate of 30 r/min. After a certain time, the mixture was filtered to obtain the desired extract.

2.2.2 Degumming process of silk
The cocoon was dried at 100 °C for 2H. Then silks were degumming in the Na2CO3 solution.

2.2.3 Bleaching process of silk
The silk was bleached in a hydrogen peroxide solution of 2% concentration. The reaction time is one hour, the reaction temperature is 60 °C.

2.2.4 Characterization of the silk surface
Scanning electron microscopy (SEM, JSM-7500F, JEOL) examined the surface morphology of silks which were treated by different process with 15 kV electron acceleration voltage.

2.2.5 The residual ratio of silk
The residual ratio of silk reflects the weight loss during the treating process of silk. The remaining ratio of silk is calculated according to the following formula.

\[ \text{residual ratio} = \left( \frac{m_2}{m_1} \right) \times 100\% \]

\( m_1 \): the weight of the raw silk.
\( m_2 \): the weight of the treated raw silk.

3 Results and discussion
3.1 Orthogonal test of cocoon degumming
In order to obtain the optimum process conditions for silk degumming, an orthogonal test was carried out. Three controllable variables, initial RB concentration (A), FeSO4 concentration (B), and H2O2 concentration(C), were set at three levels, respectively. With reference to the experimental design theory, the orthogonal array L9 (33) was selected to arrange the experiments (Table 1). The results are listed in Table 2.
Table 1 Orthogonal factor level table

| level | Alkali dosage (A)/% | Time(B)/min | The weight ratio of water/silk (C) |
|-------|---------------------|-------------|-----------------------------------|
| 1     | 0.2                 | 60          | 40:1                              |
| 2     | 0.3                 | 90          | 50:1                              |
| 3     | 0.4                 | 120         | 60:1                              |

According to the R values in Table 2, the influential order of the three factors on the residual ratio of silk degumming was A>B>C. Thus H2O2 concentration and initial RB concentration have a more important influence on the residual ratio of silk.

According to the value of k, the optimum condition was A1B1C2. However, the optimum condition of A1B1C2 did not appear in the orthogonal test. In the orthogonal test, the best condition was experiment No. (A1B1C1) and its residual ratio of silk was 92.69%.

Thus the optimum conditions were determined as follows: the concentration of Na2CO3 is 0.2%, the degumming time is 1H, and the ratio of water/silk is 40:1.

Table 2 Orthogonal table and range analysis of results

| Experimental number | serial A | B | C | Residual ratio of silk/% |
|---------------------|----------|---|---|--------------------------|
| 1                   | 1        | 1 | 1 | 92.69                    |
| 2                   | 1        | 2 | 2 | 92.01                    |
| 3                   | 1        | 3 | 3 | 91.73                    |
| 4                   | 2        | 1 | 2 | 90.95                    |
| 5                   | 2        | 2 | 3 | 90.14                    |
| 6                   | 2        | 3 | 1 | 89.78                    |
| 7                   | 3        | 1 | 3 | 89.43                    |
| 8                   | 3        | 2 | 1 | 89.09                    |
| 9                   | 3        | 3 | 2 | 88.86                    |
| K1                  | 276.43   | 273.07 | 271.56               |
| K2                  | 270.87   | 271.24 | 271.82               |
| K3                  | 267.38   | 270.37 | 271.30               |
| k1                  | 92.14    | 91.02 | 90.52                |
| k2                  | 90.29    | 90.41 | 90.61                |
| k3                  | 89.13    | 90.12 | 90.43                |
| R                   | 3.02     | 0.90 | 0.18                 |

3.2 The protective ability of GCJSY on silk protein

3.2.1 The concentration of GCJSY

In this section, GCJSY was added after the degumming process of silk to investigate its protective ability on silk protein. The results were shown in Figure 1. It can be concluded from Figure 1 that the residual ratio of silk decreased slowly with the increasing of the GCJSY’s amount. This was because while sericin was dissolved in water, the addition of GCJSY facilitated the separation of sericin from
silk fibroin. While the concentration of GCJSY reaches 0.1%, the GCJSY has no more influence on the residual ratio of silk.

Cocoons needed to be bleached after degumming, which was due to tannic acid, the pigment in the tussah silk can not be removed under alkaline condition. After the cocoons were degummed under different concentrations of GCJSY, the above cocoons were bleached by 2% H₂O₂. The result was shown in Figure 2.

According to Figure 2, the residual ratios of the silk treated by GCJSY were higher than that of the silk without GCJSY treating. And the residual ratio of the silk was increasing with the increasing of GCJSY’s concentration. While the concentration of GCJSY reached 0.08%, the residual ratio of silk reached maximum.

3.2.2 Extracting method of Camellia meal

Different exacts which were exacted from camellia meal with different modifiers were added after the degumming process of silk. The concentration of exact was controlled at 0.08%, and the results were shown in Figure 3. The least residue of silk was appeared while the silk was treated by GCJSY-NaOH.

After treated by different GCJSY, the cocoon silks were bleached at 2% hydrogen peroxide. The the residual ratio of the silks were shown in Figure 4. The residual ratio of silk treated by GCJSY-NaOH and GCJSY was 86.82% and 87.25% respectively.

3.3 Surface morphology of silk
The protective ability of GCJSY on the silk was confirmed by SEM (Figure 5). The surface appearance of silks by different treatments were different. As shown on the Figure 5 (a), there are many impurities on the silk surface. It was because silk protein could not completely dissolved in water by Na$_2$CO$_3$. And some dents were appeared on the surface of the silk fiber (Figure 5 (c)), this was mean that the silk fiber was damaged during bleaching process. Silk surface of silk treated by GCJSY was relatively clean (Figure 5 (b)). And in Figure 5 (d), the surface of the silk fiber was smoother and more tidier than the surface of the silk fiber without GCJSY treatment. This may be due to the attachment of some active ingredient inside GCJSY to the fibroin surface and play a protective role in silk fibroin fibers.

![Image of SEM pictures of silk surface](a) Silk Degumming with sodium carbonate  
(b) After the degumming of sodium carbonate, the treated silk was treated with the extract  
(c) Direct degumming of silk with sodium bleaching carbonate degumming  
(d) Degumming with sodium carbonate and of silk after GCJSY-T3 treatment

Figure 5 SEM pictures of silk surface

4 conclusion

While the concentration of GYJSY was 0.08%, the residual ratio of silk after degumming in the Na$_2$CO$_3$ solution and bleaching at 2% hydrogen peroxide was 87.2%. And the residual ratio of silk in the blank experiment was only 84.12%. The surface morphology of silk was observed by scanning electron microscope (SEM). Silk surface of silk treated by GCJSY was more smooth and neat than silk surface of silk without GCJSY treatment. It was concluded that GCJSY play protective ability during degumming process and bleaching process of silk.

References

[1] Chen H Z, Liang J, Min S J and HU G L 2002 Journal of dong hua university 3 132-136  
[1] Md.M R K, Masuhiro T, Zhang X H and Hideaki M 2013 J Mater Sci.48 3731–3736  
[2] Ma J, Wang X Y, L Q, Shi S L and Ma J B 2005 Journal of Anhui Agri Sci.33 674-675
[3] Darshil U S, David P and Fritz V 2014 Composites Science and Technology 101 173-178
[4] Akira M, Peggy C and David L K 2006 The Journal of Physical Chemistry B 110 21630-21638
[5] Subhas C.K, Biraja C D, Rupesh D and David L K 2008 Progress in Polymer Science 33 998–1012
[6] Ma L, Chen Y.Z, Peng S F, Wang X N, Chen L S, Wang R, Yang X H and Luo J 2013 Journal of Central South University of Forestry & Technology 10 34-37
[7] Li Y F, Hu L and Wang L Z 2009 Journal of Guangxi Agricultural Sciences 4 450-454
[8] Ma L and Chen Y Z 2009 Chinese Agricultural Science Bulletin.25(08):82-843.2009,40(4);450-454