韓蠶學誌 38(2), 138~143(1996)
Korean J. Seric. Sci.
<論 文>

Effect of Tartaric Acid on Cooking of Tasar Silk Cocoon (*Antheraea mylitta* D.)

Gulrajani M.L., Subrata Das, R. Chattopadhyay and Kushal Sen
Department of Textile Technology,
Indian Institute of Technology, Delhi,
Hauz-Khas, New Delhi-110 016, India

Abstract

Cooking of tasar silk cocoon of Deba variety (*A.mylitta D.*) with tartaric acid has been optimized by using an orthogonal central composite design. Shell weight loss and silk filament recovery are influenced by duration of treatment and acid concentration. Mechanical properties do not change with the process parameters. Hardness of water does not affect significantly the recovery of silk filament.

Key words : *Antheraea mylitta* D., Cooking, Daba, Silk recovery.

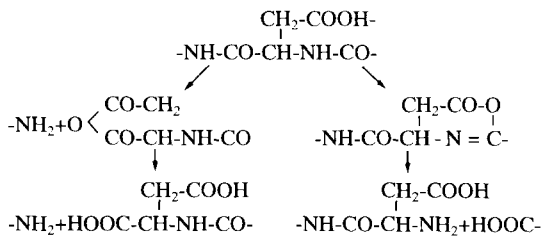
INTRODUCTION

Cooking of tasar cocoon entails the softening of gummy component of silk protein to achieve trouble free unravelling of filaments from cocoon shell. The treatment differs from mulberry due to the presence of tannins and calcium oxalate in tasar silk which form strong complexes, thereby inhibiting softening of cocoon in boiled water (Tikoo, B.L. and Goel, R.K., 1987).

Tasar cocoon (Daba) cooking has been the subject of many recent investigations (Das, S. *et al.*, 1992, 1994, Sonwalkar, T.N., 1985 and Gulrajani, M.L. *et al.*, 1995) During cooking the gummy component of silk, i.e. sericin, is removed partially by hydrolytically breaking it into smaller water soluble fractions, such as amino acids and oligomers of amino acid. Cooking can be carried out by treating tasar cocoons with alkalis (Das, S. *et al.*, 1994) enzymes (Sonwalkar, T.N., 1985) amines (Gulrajani, M.L. *et al.*, 1995) or even with hydrogen peroxide (Das, S. *et al.*, 1992) prior to reeling. Although degumming of silk with organic acids has been reported in the literature (Gulrajani, M.L., 1992a), no systematic effort is made to cook tasar cocoon with organic acids.

Tasar silk cocoon needs gradual action during cooking owing to weak peduncle end. Otherwise, during cooking the peduncle end bursts open thereby resulting in entanglement of filament during unwinding from cocoon and ultimately registers poor silk recovery. The action of various degumming agents has been comprehensively covered in the literature (Gulrajani, M.L., 1992b).

The present study is aimed at optimising the cooking conditions of tasar silk cocoon with tartaric acid using an orthogonal central composite design. Tartaric acid was selected as the process of degumming proceeds very gradually with time. the degumming action of acid has been proposed to be due to the hydrolysis of proteins at aspartic and glutamic acid residues (Chopra, S. and Gulrajani, M.L., 1994). The mechanism of acid hydrolysis of proteins as postulated by Blackburn and Lee (Blackburn, S and Lee, G.R., 1954) is shown in scheme 1.



Scheme. 1.

The effect of hardness of water on tartaric acid cooking has also been studied.

MATERIALS AND METHODS

Stifled and sorted grey Daba cocoons were selected for the study. These cocoons were grown on Terminalia arjuna under tropical climatic zone in India. The specifications of the cocoon lot is given below:

Source : Raw Material Bank, Central Silk Board, Chaibasa, Bihar, India.
Colour : Grey
Shape : Oval
Voltinism : Bivoltine
Average cocoon weight(Stifled) : 3.5 g
Average filament length : 600 m
Average non-broken filament length : 130 m
Average filament fineness : 9 denier (0.999 tex)

Laboratory grade Tartaric acid [purity 99%] was used in the experiments.

1. Cooking

Daba cocoons were conditioned for 48 h (27°C and 65% R.H.). These were subsequently cooked at 95°C with 7.46-12.54 g/*l* tartaric acid. Liquor ratio was kept at 30:1 and the pH was 2.35 in all the cases. The time of treatment was varied as per the experimental design. The cooked silk cocoons were squeezed and deflossed to locate the true end of the filament. The deflossed cocoons were reeled on a wrap reel. The hanks of silk silament were taken out and coditioned before testing for various properties. Silk waste generated during the reeling process was collected, conditioned and weighed.

2. Experimental design

The process parameters selected as independent variables were : treatment time (x_1) and concentration of tartaric acid (x_2), with five levels for each variable (Table 1). The experiments were planned according to an orthogonal two factor central composite design with five centre points and an axial spacing of ± 1.27 (Morgan Ed., 1991). Thus a set of 13 experiments were performed. The treatment conditions are given in Table 2.

Table 1. *Experimental design*

Variable	Level				
	-1.27	1	0	+1	+1.27
x_1(min)	27.30	30	40	50	52.70
x_2(g/*l*)	7.46	8	10	12	12.54

x_1=Time of treatment
x_2=Concentration of acid

Table 2. *Observed and calculated values at different treatment conditions*

Expt. No.	Time (min)	Acid conc. (g/*l*)	Silk recovery(%)	Shell weight loss(%)
1	50	12	63.83	17.88
			(61.45)	(17.55)
2	50	8	52.35	14.59
			(54.14)	(13.46)
3	30	12	48.46	10.12
			(45.55)	(11.14)
4	30	8	38.42	6.25
			(38.24)	(7.05)
5	52.70	10	63.36	15.61
			(63.51)	(16.79)
6	27.30	10	41.19	10.05
			(43.31)	(8.65)
7	40	12.54	45.43	14.50
			(48.68)	(14.22)
8	40	7.46	41.58	8.49
			(39.40)	(9.03)
9	40	10	38.11	12.16
			(44.04)	(11.62)
10	40	10	44.92	11.76
			(44.04)	(11.62)
11	40	10	44.45	12.55
			(44.04)	(11.62)
12	40	10	49.57	12.41
			(44.04)	(11.62)
13	40	10	42.83	9.63
			(44.04)	(11.62)

Figures in parenthesis indicate calculated responses

3. Evaluation of properties

1) Shell weight loss

The shell weight loss (%) was calculated as:

Shell weight loss (%) = $[(W_1-W_2)/W_1] \times 100$

where,

W_1=Weight of cocoons before cooking
W_2=Weight of cocoons after cooking

2) Silk recovery

The raw silk recovery was calculated as per the following relation:

Silk recovery (%)=[A/(A+B)]×100

where,

A=Weight of reelable filament

B=Weight of silk waste generated during reeling.

3) Tensile properties

Tensile properties such as tenacity, breaking extension and modulus of raw silk yarns were evaluated using Instron Universal Tensile Testing machine (model 4301) interfaced with a computer. The following specifications were used:

Cross-head speed - 15 cm/min

Gauge length 20 cm

An average of 30 observations has been reported.

4) Analysis of data

A quadratic polynomial was used to analyse the relaionship between the measured responses and the process parameters (Eqn. 1):

$$y = b_0 + \sum_{i=1}^{2} b_i x_i + \sum_{i=1}^{2} b_{ii} x_i^2 + \sum_{i=1}^{2} b_{ij} x_i x_j \qquad (1)$$

where y is the measured response, x is the process parameter, b_0, b_i, b_{ii} and b_{ij} are the coefficients of the regression equation and i and j are integers with i<j. To test the estimated regression equation for closeness of fit, the Fisher F-test was employed. The estimated coefficients of the regression equation were tested for significance using t-test. The insignificant coefficients were deleted form the equation and those remaining were recalculated and the closeness of fit reassessed. Three dimensional surface responses were plotted to study the effect of variables on the silk recovery and shell weight loss. The optimum degumming condition was determined and experiment was repeated thrice at this condition to check for reproducibility.

RESULTS AND DISCUSSION

The observed and calculated values of the various properties for all the 13 experiments are given in Table 2 and 3. The values of coefficients of the regression equations 'b', F-ratio, the adjusted squared multiple correlation coefficient and standard error of estimate for all the responses are given in Table 4.

Table 3. *Observed values at different treatment conditions*

Expt. No.	Time (min)	Acid conc. (g/l)	Tenacity (N/tex)	Modulus (N/tex)	Elongation at break(%)
1	50	12	0.20	5.74	21.80
			(17.52)	(19.73)	(23.53)
2	50	8	0.24	6.24	22.38
			(23.80)	(15.84)	(28.01)
3	30	12	0.25	6.65	25.45
			(19.83)	(15.06)	(26.48)
4	30	8	0.26	6.82	23.93
			(17.38)	(18.50)	(22.90)
5	52.70	10	0.22	5.68	24.85
			(17.24)	(15.56)	(16.25)
6	27.30	10	0.25	6.26	25.93
			(22.24)	(26.13)	(24.41)
7	40	12.54	0.22	6.54	21.97
			(22.38)	(24.48)	(30.80)
8	40	7.46	0.19	5.58	21.45
			(16.37)	(23.85)	(18.91)
9	40	10	0.22	6.43	22.06
			(21.71)	(28.07)	(20.90)
10	40	10	0.21	7.11	18.86
			(20.72)	(18.03)	(23.96)
11	40	10	0.23	7.75	19.45
			(18.29)	(13.10)	(20.16)
12	40	10	0.22	7.70	19.03
			(21.54)	(13.03)	(25.30)
13	40	10	0.23	7.42	21.53
			(14.14)	(19.69)	(13.52)

Figures in square brackets indicate the CV(%)

1. Silk recovery

3-D spatial diagrams of the response surfaces in respect of silk recovery has been depicted in Fig. 1. It is noticed that the silk recovery increases with increase in acid concentration and duration of treatment. However, the effect of treatment time is predominent over acid concentration. The rate of increase of silk recovery is rapid beyond 40 min treatment time and 10 g/l tartaric acid concentration. The increase in silk recovery is attributed to the substantial removal of gummy substances and uniform softening of cocoon shell, thereby resulting in more amount of reelable filament in comparison to silk waste.

Table 4. *Coefficients of regression equations*

Coefficient	Shell weight loss (%)	Silk recovery (%)	Tenacity (N/tex)	Modulus (N/tex)	Breaking extension(%)
b_0	11.623	44.040	0.218	7.234	20.258
b_1	3.204	7.951	-0.015	-0.308	-0.909
b_2	2.045	3.655			
b_{11}	0.680	5.809	0.014	-0.590	2.894
b_{22}				-0.534	0.612
b_{12}			-0.008		
F-ratio	25.573	20.742	4.318	4.819	11.635
R	0.860	0.832	0.453	0.488	0.727
Std error	1.180	3.421	0.015	0.523	1.212

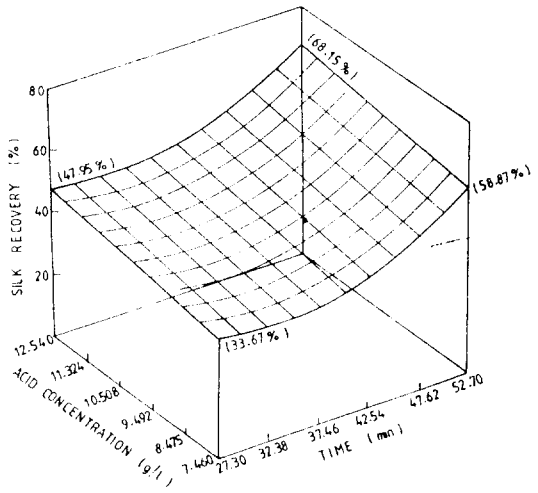


Fig. 1. *Spatial diagrams of silk recovery against time of treatment and tartaric acid concentration at 95°C.*

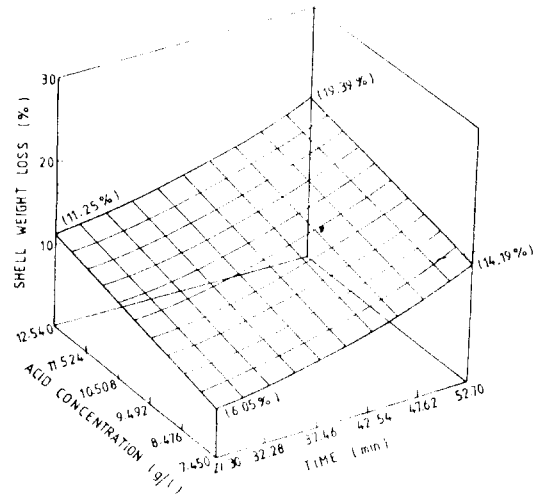


Fig. 2. *Spatial diagrams of shell weight loss against time of treatment and tartaric acid concentration at 95°C.*

2. Shell weight loss

It is apparent from Table 4 that the shell weight loss is affected by two independent variables, and it showed good correlation with these process parameters. Spatial diagrams of the response surface were drawn based on the data from Table 4 and are reproduced in Fig. 2. This shows that increase in the shell weight loss occurs with increase in acid concentration and duration of treatment. The maximum shell weight loss (19%) is obtained with 12.54 g/*l* acid concentration and 52.70 min duration which corresponds to maximum removal of sericin and inorganic matters from the tasar cocoon.

3. Correlation between silk recovery and shell weight loss

The regression analysis was carried out with silk recovery as the independent variable and shell weight loss as dependent variable. Silk recovery showed excellent correlation with shell weight loss. This is due to the removal of sericin and other inoganic substances from the tasar cocoon shell in cooking with tartaric acid and subsequent softening phenomena under the range studied, leading to more recovery of tasar filament in comparison to silk waste. As a result, the silk recovery increases with increase in shell weight loss. The regression eqution is as follows:

Silk recovery=21.169+2.35 × Shell weight loss

R=0.91, S.E.=2.90, F-ratio=249.36

Fig. 3 shows how the silk recovery varied with change in shell weight loss.

4. Tenacity, breaking extension and initial modulus

Poor correlation was observed between the tenacity ans modulus of tasar filament with the influencing factors; thus no best fit model was obtained. The tenacity and modulus varied within the range of 0.19 N/tex-0.26 N/tex and 5.68 N/tex-7.75 N/tex, respectively. Though a fair correlation was observed between breaking extension with the influencing factors but considering the very little change in the range of values (18.86%-25.93%) the effect was ignored. A high inherent variation in the mechanical properties were reflected in the CV% values. This is due to natural variation in tasar cocoon filament.

5. Optimization

To determine the optimum treatment condition, one dependent variable, i.e., the silk recovery, was considered. Values for the complete set of 25 experiments were calculated from the best fitted regression equations and the data obtained were thereby ranked. Since the cocoons bursted open at the peduncle end as well as become oversoft at the conditions derived from the calculated experiments for rank 1 and rank 2, the reeling was not possible. Thus the experiment related to rank 3 was performed and repeated thrice. The result obtained is presented in Table 5. The following cooking condition is recommended:

Tartaric acid-10 g/*l*

Temperature-95°C

Time-52.70 min (50-55 min)

Liquor ratio-30:1

6) Effect of hardness of water

In order to study the effect of hardness of water on the silk recovery from tasar cocoons, experiments were carried out on Daba tasar cocoons in water of varying hardness. The water of diffrent hardness were prepared according to IS:5785. The actual hardness was determined by EDTA titriometric method. Cooking was performed with tartaric acid at the optimised conditions.

Table 5. *Results of experiment performed under optimum condition*

Optimum condition	Silk recovery(%)
52.70 min 95°C 10 g/*l* tartaric acid	59.78

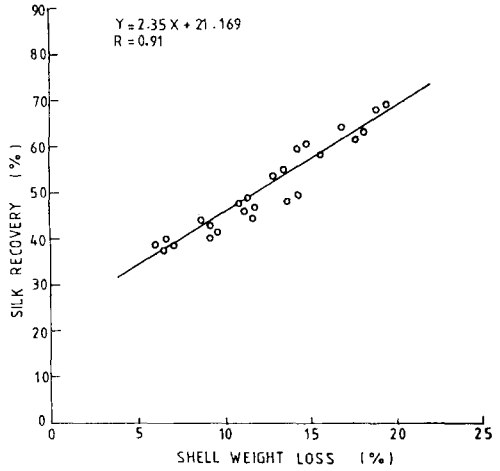


Fig. 3. *Plot of silk recovery against shell weight loss.*

Table 6. *Effect of hardness of water on silk recovery*

Hardness(ppm)	Silk recovery(%)
0	59.78
520	57.26
1100	56.42
2780	55.91

The results (Table 6) show that the hardness of water has practically no effect on silk recovery.

CONCLUSIONS

Tartaric acid has been shown to be effective for use in cooking of Daba tasar cocoons. The hardness of water has no effect on cooking with tartaric acid.

ACKNOWLEDGEMENTS

The authors acknowledge with thanks the financial support provided by the Central Silk Board, Ministry

of Textiles, Govt. of India under the National Sericulture Project to carry out the work.

적 요

인도 Daba 작잠 품종 고치에 대하여 주석산을 이용한 고치 삶기 방법의 적정화가 시도되었는데 고치층 감모율과 고치의 실켜기 길이는 주석산 처리 시간과 처리농도에 영향을 받았지만 고치실의 기계적 성질은 처리 조건 범위 내에서 차를 보이지 않았다. 또한 고치 삶기 용수의 경도는 작잠고치의 실켜기 길이에 크게 영향을 주지 않았다.

REFERENCES

Blackburn S and Lee G.R.(1954) The liberation of aspartic acid during the acid hydrolysis of proteins, *Biochem. J.*, **58**:227.

Chopra S and Gulrajani M.L. (1994) Comparative evaluation of the various methods of degumming silk, *Indian J. Fib. & Textile Res.*, **19**:22.

Das S. et al. (1992) An improved method of tussah silk reeling, *J. Textile Inst.*, **83**:280.

Gulrajani M.L. (1992a) Some studies in degumming of silk with organic acids, *J. Soc. Dyers Colour.*, **108**:60.

Gulrajani M.L. (1992b) Degumming of silk, *Rev. Prog. Coloration.*, **22**:79-89.

Gulrajani M.L. et al. (1995) Studies on cooking (partial degumming) of tussah silk cocoon, *Indian J. Fib. & Textile Res. communicated.*

Morgan Ed. (1991) Chemometrics : Experimental Design, John Wiley & Sons Ltd., Chichester, West Sussex, England, 241-248.

Sonwalkar T.N. (1985) Silk reeling and handicrafts, *Sericologia*, **25**:191.

Tikoo B.L. and Goel, R.K. (1987) Wet system of reeling in oak tasar silk industry, *Indian Silk*, **26**:23.