

# STUDIES ON STRUCTURE - PROPERTY CORRELATION IN SOME VARIETIES OF INDIAN SILK

by

**K. MURUGESH BABU**

**Textile Technology Department**

Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the



**Indian Institute of Technology, Delhi**

**July, 2001**

I. I. T. DELHI.  
LIBRARY  
Acc. No. TH-337

I. I. T. DELHI  
LIBRARY  
EXCESSED

TH  
677.37(540)  
MUR-S

## CERTIFICATE

This is to certify that the thesis entitled "**Studies on Structure-Property Correlation in Some Varieties of Indian Silk**", being submitted by **Mr. K. Murugesh Babu** to the Indian Institute of Technology, Delhi, for the award of the degree of **Doctor of Philosophy** in the **Department of Textile Technology**, is a bonafide research work carried out by him. Mr. Murugesh Babu has worked under my guidance and supervision and fulfilled the requirements for submission of the thesis.

The results contained in this thesis have not been submitted, in part or full, to any other University or Institute for the award of any degree or diploma.



**Prof. Kushal Sen**  
Department of Textile Technology  
Indian Institute of Technology, Delhi  
New Delhi-110016

## ACKNOWLEDGEMENTS

I wish to express my deep sense of gratitude to my supervisor, Prof. Kushal Sen for his invaluable guidance, encouragement and constant support throughout the course of this research work. Working under him has been an extremely fruitful experience in ways more than one.

I extend my sincere thanks to Prof. B.L. Deopura and Prof. R.B. Chavan, the present and previous Heads of the Department respectively, for their co-operation, and help during the course of this research work.

I express my sincere thanks to Prof. V.B. Gupta and Prof. P. Bajaj for their guidance and timely suggestions during this research work.

Thanks are due to the technical staff of Textile Chemistry Laboratory, Mr. V.A. Passi, Mr. Rajendra Prasad, Mr. Shiv Charan, Mr. Prakash Chand, Mr. Jagadish and Suresh for their help and cooperation; to Mr. Bharadwaj, Mr. Padam, Mr. Rajkumar, Mr. Khattar and Mr. Khanna and Mr. Amarjeet for their help and assistance in various ways.

I wish to express my heartfelt thanks to my friends and colleagues, Dr. Sampath Kumar, Dr. Sreekumar, Dr. Prabir Kar, Dr. Mahendra Gowda, Dr. Shipra Kumari, Mr. Shirish Kumar and Ms. Ruchira Gupta for their support and assistance during the course of this research work.

I thank the Bapuji Educational Association, the Principal, BIET, Davangere for sanctioning me the study leave to carry out this research work at IIT, Delhi.

I take this opportunity to thank my parents, brother, mother-in-law and brother-in-laws for their support and cooperation through out this work. Last but not the least, I am extremely thankful to my wife Shilpa and daughter Sheema who always stood by me through out this research work.

  
**K. MURUGESH BABU**

## ABSTRACT

Silk, the only natural fibre available in the filament form has been known for its lustre, sheen, handle and good mechanical properties. Unique characteristics such as scroopiness and rich aesthetics are the reasons for its status among the textile fibres. India being the second largest producer of silk in the world has a great potential for the export of silk, silk articles and garments. It is felt that an understanding of the structure and properties of different varieties of Indian silk through a proper scientific study would go a long way to serve the needs of this industry.

The present thesis is a compilation of the detailed investigations on the structure and properties of five varieties of Indian silk, two mulberry and three non-mulberry, with a major emphasis on the correlations between their structure and properties.

The broad framework of the thesis has been designed on the following premise:

*"The mechanical properties and relaxation parameters of silk in general depend on the microstructural morphology which in turn must depend upon the chemical architecture of the fibres. The dyeing behaviour too must be governed by some of the above structural and molecular characteristics".*

This means that it should be possible to establish some correlation between various structural features of silk fibres and the properties thereof.

The first part of the study involving the measurement of the macro characteristics, such as filament length, degumming loss, denier, cross-section, moisture regain etc. reveals significant differences among the different varieties. Interestingly, large differences have been observed in all these parameters along the

filament length also. It is observed that while the denier of the filament decreases considerably from the outer to the inner layers, the density increases concomitantly. Surprisingly, the gum content in outer layers is considerably higher than that found in the inner layers of cocoons and reduces gradually as one moves towards the inner layers. Compared to non-mulberry varieties the mulberry silks demonstrate lower moisture regain. This too is found to reduce as one moves from the outer to the inner layers. Electron micrographs of all the non-mulberry varieties show micro voids.

In the next part of the study the amino acid composition of the different varieties using reverse phase HPLC technique has been determined and analysed. In both the varieties of mulberry silk, glycine, alanine and serine constitute about 82% of the amino acids, while in the non-mulberry variety, these are about 73% with a very high proportion of alanine. The non-mulberry varieties show a substantial proportion of amino acids with bulky side-groups. The higher hydrophilic to hydrophobic amino acid ratio (0.35-0.44) has been shown to be responsible for higher moisture content of non-mulberry silks. Cystine and methionine are present in all the varieties. The higher intrinsic viscosity of non-mulberry varieties suggests higher molecular weight of these varieties. It has been established that there is no difference in chemical architecture between the outer and inner layers of cocoons, despite differences seen in the macro-characteristics.

Microstructural analysis involving measurement of crystallinity, crystallite size, crystallite orientation, birefringence, sonic modulus and dichroic ratio, reveals that all the microstructural parameters substantially increase from the outer to the inner layers. As expected, different varieties of silk differ in respect of the above structural parameters, however, despite genetically being different, the three non-mulberry varieties demonstrate striking similarities in terms of crystal structure and

molecular architecture as determined by FTIR. The WAXD spectra of all the non-mulberry varieties shows two major diffraction peaks at  $2\theta$  value of  $17^\circ$  and  $21^\circ$  as against one for mulberry at  $2\theta$  value of  $20.5^\circ$ . Similarly, the FTIR spectra at  $0^\circ$  polarizer angle shows one peak at  $965\text{ cm}^{-1}$  for all the three non-mulberry as against two peaks at  $998\text{ cm}^{-1}$  and  $976\text{ cm}^{-1}$  for the mulberry variety. Higher alanine content as also more amount of bulky amino acid residues do seem to play a definite role.

The tensile properties, viz., tenacity, elongation and initial modulus too have been found to vary substantially along the length of the filament. The tenacity and the initial modulus increase while the extension-at-break reduces in all the varieties as one move towards the inner layers. Typical stress-strain behaviour showing a characteristic yield point has been observed in all the three non-mulberry varieties. It has been observed that within a single variety the mechanical properties and the structural parameters correlate exceedingly well. The global correlation involving all the varieties is not good. However, if one segregates these into two groups (mulberry and non-mulberry), the group wise correlations are excellent.

All the silk varieties show the inverse stress relaxation behaviour. Interestingly, the stress relaxation and inverse stress relaxation rates have been found to give very good global correlation with the structural parameters even when all the varieties are taken together. The higher is the crystallinity, the lower is the magnitude of the relaxation rate; the sign depends on the nature of relaxation.

These silk groups behave differently to the thermal inputs too. The DTA thermograms (under nitrogen) of mulberry silk fibres exhibit a first broad endotherm at around  $62^\circ\text{C}$  due to the evaporation of water. Thereafter, these fibres are stable upto about  $280^\circ\text{C}$ , followed by a prominent endothermic peak at around  $320^\circ\text{C}$ , which may be associated with onset of decomposition. As against the mulberry silks, all the three

non-mulberry silk fibres exhibit two more transitions at around 230°C and 300°C respectively, may be associated with some molecular rearrangement, followed by a major decomposition peak at around 368°C. TGA and DSC analysis also substantiates these observations.

The studies related to dyeing clearly demonstrate the differences in dye uptake between the varieties as also within a variety. The inner layers take up less dye irrespective of the fibre. In general, the two mulberry varieties exhibit higher dye uptake compared to non-mulberry varieties. Among the three non-mulberry varieties, muga seems to be more resistant to the adsorption of dyes. The results of the dye uptake measurements have been correlated with the end amino groups and the intrinsic viscosity of the different silk fibres.

# CONTENTS

Topic	Page No.
Certificate	(i)
Acknowledgements	(ii)
Abstract	(iii)
List of Figures	(iv)
List of Tables	(v)

## CHAPTER 1 INTRODUCTION AND REVIEW OF LITERATURE

1.1	INTRODUCTION	1
1.2	REVIEW OF LITERATURE	2
1.2.1	Silk - The fibre	5
	1.2.1.1 Average filament length	6
	1.2.1.2 Shape and surface texture	7
	1.2.1.3 Fibre fineness	7
1.2.2	Chemical structure	8
	1.2.2.1 Molecular structure	8
	1.2.2.3 Amino acid composition of fibroin	10
	1.2.2.4 The $\alpha$ and $\beta$ forms of molecules	16
1.2.3	Sericin	17
1.2.4	Microstructure and morphology	20
	1.2.4.1 Crystal structure	21
	1.2.4.2 WAXD Spectra and Crystallinity in silk fibres	23
	1.2.4.3 IR-Spectroscopy	27
	1.2.4.4 Crystal size	30
	1.2.4.5 Orientation	33
1.2.5	Mechanical Properties	37
	1.2.5.1 Tenacity, elongation and modulus	37
	1.2.5.2 Stress-strain characteristics	40
	1.2.5.3 Creep and stress relaxation	42

1.2.5.4	Inverse stress relaxation	43
1.2.5.5	Dynamic Mechanical Behaviour	44
1.2.6	Thermal behaviour	47
1.2.7	Dyeing behaviour of silk	53
1.2.8	Epilogue	59

## **CHAPTER 2      MACRO CHARACTERIZATION OF DIFFERENT VARIETIES OF SILK**

2.1	INTRODUCTION	61
2.2	EXPERIMENTAL	62
2.2.1	Materials	62
2.2.2	Sample preparation	62
2.2.2.1	Cooking	62
2.2.2.2	Reeling	63
2.3	EVALUATION	63
2.3.1	Average filament length	63
2.3.2	Degumming loss (%)	63
2.3.3	Linear density	64
2.3.4	Scanning Electron Microscope Studies	64
2.3.4.1	Longitudinal and cross-sectional shape	64
2.3.4.2	Fracture studies	64
2.3.5	Density	65
2.3.6	Moisture regain	65
2.4	RESULTS AND DISCUSSION	65
2.4.1	Filament length	65
2.4.2	Degumming loss (%)	66
2.4.3	Filament denier	68
2.4.4	Cross-sectional shape	70
2.4.5	Density	74
2.4.6	Fracture studies	76
2.4.7	Moisture regain	79
2.5	CONCLUSIONS	80

## **CHAPTER 3 ANALYSIS OF AMINO ACID COMPOSITION**

3.1	INTRODUCTION	81
3.2	EXPERIMENTAL	84
3.2.1	Materials	84
3.2.1.1	Fibre samples	84
3.2.1.2	Chemicals used	84
3.2.2	Sample preparation	85
3.2.3	HPLC analysis	85
3.2.3.1	Hydrolysis of silk	85
3.2.3.2	Drying and redrying	86
3.2.3.3	Derivatization with PITC	86
3.2.3.4	Separation of amino acids	86
3.2.4	Determination of Intrinsic viscosity	87
3.3	RESULTS AND DISCUSSION	88
3.3.1	Amino acid composition and analysis	88
3.3.2	Morphology and Chemical architecture	96
3.3.3	Effect on moisture regain	96
3.3.4	Intrinsic viscosity	97
3.4	CONCLUSIONS	100

## **CHAPTER 4 MICRO STRUCTURE AND PROPERTY CORRELATION**

4.1	INTRODUCTION	101
4.2	EXPERIMENTAL	102
4.2.1	Materials	102
4.2.2	Sample preparation	102
4.2.3	Evaluation	103
4.2.3.1	Mechanical Properties	103
4.2.3.2	Fibre characterization	103
4.2.3.2.1	X-ray crystallinity	103
4.2.3.2.2	Preparation of amorphous sample	103
4.2.3.2.3	Crystallite size	104

	4.2.3.2.4 Crystallite orientation function	104
	4.2.3.3 FTIR-Dichroic ratio	104
	4.2.3.4 Birefringence	105
	4.2.3.5 Sonic Modulus	105
4.3	RESULTS AND DISCUSSION	105
	4.3.1 Mechanical Properties	105
	4.3.2 WAXS Studies	113
	4.3.3 FTIR-Spectroscopy	119
	4.3.3.1 Dichroic ratio	120
	4.3.4 Birefringence and Sonic modulus	122
	4.3.5 General Correlations	127
4.4	CONCLUSIONS	128
<b>CHAPTER 5</b>	<b>STRESS RELAXATION AND INVERSE STRESS RELAXATION BEHAVIOUR</b>	
5.1	INTRODUCTION	129
5.2	EXPERIMENTAL	131
	5.2.1 Materials	131
	5.2.2 Determination of Inverse Stress Relaxation Index	131
5.3	RESULTS AND DISCUSSION	132
	5.3.1 Correlation with morphological structure	139
5.4	CONCLUSIONS	142
<b>CHAPTER 6</b>	<b>THERMAL CHARACTERIZATION AND ANALYSIS</b>	
6.1	INTRODUCTION	143
6.2	EXPERIMENTAL	145
	6.2.1 Materials	145
	6.2.2 Sample preparation	145
	6.2.3 Thermogravimetric analysis	145
	6.2.4 Differential Thermal Analysis	145
	6.2.5 Differential Scanning Calorimetry	145

6.3	RESULTS AND DISCUSSION	145
6.3.1	Thermogravimetric analysis	146
6.3.2	Differential Thermal Analysis	151
6.3.3	Differential Scanning Calorimetry	155
6.4	CONCLUSIONS	159
<b>CHAPTER 7</b>	<b>EFFECT OF STRUCTURE ON DYEING BEHAVIOUR</b>	
7.1	INTRODUCTION	160
7.2	EXPERIMENTAL	162
7.2.1	Materials	162
7.2.2	Chemicals used	162
7.2.3	Dyeing	163
	7.2.3.1 Dyeing with Acid dyes	163
	7.2.3.2 Dyeing with Disperse dyes	163
7.2.4	Evaluation of dyed Samples	164
	7.2.4.1 Determination of Exhaustion (%)	164
	7.2.4.2 Estimation of Dye content on fibre	164
	7.2.4.3 K/S	165
7.2.5	Estimation of end amino groups in silk	165
	7.2.5.1 Theory	165
	7.2.5.2 Preparation of Ninhydrin Solution	167
	7.2.5.3 Preparation of Glycine Standard solution	167
	7.2.5.4 Silk-Ninhydrin reaction	168
	7.2.5.5 Calibration with Glycine	168
	7.2.5.6 Determination of amino groups in silk	168
7.3	RESULTS AND DISCUSSION	169
7.3.1	Response of different silks to acid dye uptake	169
	7.3.1.1 Anomalous dyeing Behaviour of silk	176
7.3.2	Response of different silks to disperse dyes	177
7.4	CONCLUSIONS	180
	<b>SUMMARY AND CONCLUSIONS</b>	181
	<b>REFERENCES</b>	185