STUDIES IN DEGUMMING OF SILK

by

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CERTIFICATE

This is to certify that the thesis entitled " **Studies in Degumming of Silk**" being submitted by **Ms. Sheetal Sethi Chopra** to the Indian Institute of Technology, Delhi, for the award of **Degree of Philosophy** is a record of bonafide research work carried out by her under my guidance and supervision.

To the best of my knowledge this thesis has reached the required standard. The material presented in this thesis, in part or full has not been submitted to any other University or any other Institute for the award of degree or diploma.

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ABSTRACT

Natural silk as extruded by the silkworm consists of two proteins namely fibroin and sericin. Degumming process separates the silkgum (i.e. sericin) from the silk filament (fibroin). Presence of sericin makes the silk coarse, lacking lustre thus concealing the very merits of silk. Removal of sericin results in the improvement of lustre as well as softness and feel of the fabric. Thus its removal becomes imperative. The proper execution of this basic finishing process becomes very essential to obtain the desirable dye uptake potential, tensile strength and handle properties in the final product.

Though both sericin and fibroin are proteins, they differ considerably in their chemical composition as well as accessibility. Sericin has much higher proportion of polar amino acids. This difference in composition makes sericin more soluble than fibroin. During the process of degumming, the hydrolysis of peptide bonds of sericin takes place and it subsequently gets removed by solubilisation or dispersion. Hydrolysis of sericin can be carried out by use of alkali, soap, acids, enzymes or even with water at high temperature. Of all these methods, soap and alkali based methods have been predominantly used and extensively studied and fewer attempts have been made to investigate other degumming agents. Hydrolysis of proteins by soap and alkali is random and non specific so chances of degradation of silk are greater if proper control is not exercised. Thus there is a need to look for alternative degumming agents which hydrolyse proteins at specific amino acids which are found in higher proportion in sericin.

The present study investigates in detail, the use of organic acids and enzymes as alternative degumming agents; comparative evaluation of various degumming agents and methods in terms of degumming efficiency and properties obtained; objective evaluation of handle properties of silk after degumming by measurement of mechanical properties; amino acid analysis of different varieties of mulberry silks and the effect of degumming agent on amino acid composition.

Silk fabrics are generally subjected to finishing treatment with acids to impart lustre and scroop. The degumming action of acids is apparently due to the hydrolysis of

proteins at certain specific amino acid residues. The proportion of these amino acids is greater in the case of sericin than fibroin. Degumming of two types of silk substrates has been carried out with organic acids and conditions for their use have been optimised. Effect of temperature, treatment time and concentration of tartaric acid has been studied using a factorial design. The weight loss, tenacity and elongation have been studied for both yarn and fabric. Flexural rigidity has also been measured in the case of yarns. Scanning Electron Microscopic studies for evaluation of surface degradation have also been carried out. Results show that most of the gum is removed during the initial 30 min of treatment time. At 100°C substantial weight loss was observed on degumming with water itself. The most effective pH range for degumming has been found to be 2.2-3.5. Use of higher temperatures and higher concentration of acid results in decrease in tenacity. The optimum degumming conditions have been found to be 8 gpl tartaric acid used at 110°C for 30 min. Studies with other organic acids have been carried out at a temperature 100°C using an acid concentration of 0.05 mol/l for a treatment time of 60 min. Weight loss, flexural rigidity and tenacity of the degummed samples have been measured. Strength of the acids (pK_a values) seem to have little effect on weight loss in the case of dibasic and hydroxy acids, however, chloroacetic acids registered variation. Considering weight loss and tenacity together, succinic acid gave the best results followed by tartaric and monochloroacetic acid.

Degummase is a bacterial protease produced by a strain of *Bacillus subtilis*. This enzyme has been studied as an alternative degumming agent using a long liquor as well as a pad-store method. The effect of treatment with Degummase on weight loss, bending length, crease recovery and strength of mulberry silk fabric has been studied and the conditions of degumming have been optimised. For the long liquor method, best degumming in terms of sufficient weight loss and minimum degradation is achieved when the silk fabric is treated with 10% enzyme (owf) at 50°C for 60 min. Good correlation has been observed between the process parameters and properties studied.

Pad-store method has been investigated to economise on the quantity of enzyme required for effective degumming. Treatment with 0.5% enzyme (owf) has been found to be optimum. At this concentration experiments were carried out by varying the

temperature and time. This method resulted in some amount of strength loss when the weight loss achieved by the pad-store and long liquor methods was almost comparable. Scanning electron microscopic (SEM) studies were carried out to assess the extent of damage. For the pad-store method optimum degumming conditions worked out to be 0.5% enzyme (owf) to be used at 50°C for 5-6 h.

A comparative evaluation of five degumming methods has been carried out. These included Tartaric acid (0.5 M), Na_2CO_3-$NaHCO_3$ buffer (0.05N), Marseilles soap (25% owf), Alcalase enzyme (10% owf) and Ethylene diamine (EDA) (0.025M). The degumming was carried out at 93°C for time periods ranging from 1 min to 2 h to study the kinetics of degumming. The rates of degumming was determined for the various methods. Per cent residual sericin has also been calculated for each silk.

The alkaline degumming agents (soap, alkali and amine) are able to degum all the three varieties of silk almost completely. Degumming with soap results in complete removal of sericin but the process is not very economical. Acidic degumming is not satisfactory at the temperature used. It is possible to accelerate the process of degumming in the case of EDA by addition of an electrolyte.

Considering all the properties together, degumming with amine is most satisfactory followed by alkaline degumming.

The three varieties of mulberry silk yarns used for the comparative evaluation of degumming agents have been subjected to amino acid analysis to determine the composition. Reverse phase HPLC has been carried out to separate the amino acids. The silks have been subjected to treatment with soap, alkali buffer and tartaric acid to separate sericin from fibroin. Hydrolysis of the fibroins has been carried out by 6N HCl as well as methanesulphonic acid (MSA). The compositions obtained for the three silks are quite comparable to the reported values. Alkaline degumming agents have resulted in some marginal losses of certain amino acids such as cystine, serine and threonine. Acid degumming does not result in any significant deviations in the yields of amino acids obtained.

Method of hydrolysis does result in some minor deviations. MSA hydrolysis resulted in a more complete analysis since quantification of tryptophan was possible by this method of hydrolysis.

Changes in mechanical and physical properties obtained by treatment of mulberry silk fabric with 5 degumming agents (acid, alkali, soap, enzyme and triethylamine) has been studied.

Low stress mechanical properties have been measured using the KES-F system. Primary hand values have been calculated from the basic mechanical properties. Results obtained for each degumming agent have been compared with those of soap treated sample and t-test has been carried out for significance of difference. In terms of low stress mechanical properties alkali and amine degumming methods are quite comparable to soap treatment. In the case of acidic and enzymatic methods, removal of gum from the interlacing areas of warp and weft is a limitation which gets reflected in the shear properties. This has been confirmed by SEM studies.

There is maximum retention of strength in the case of enzyme and amine treated samples. In soap and alkali based methods there is accompanied strength loss. Soap and alkali degummed samples rate higher in terms of softness, flexibility and scroopy feel. Enzyme and amine treated samples however, show maximum whiteness. No appreciable differences could be obtained in crease recovery as well as bending length among the differently treated fabrics.

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