The Golden Hued Muga Silk – Studies on degumming, surface modification and pigmentation profile

AN ABSTRACT
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ABSTRACT

Silk considered as the queen of textiles is well known for its elegance, strength, luster, elasticity and compatibility. Silk fiber holds an esteemed position as an elegant material in human civilization. Despite the triumphal advance of synthetic fibers, silk the most lavishing fiber bestowed by nature continues to occupy its special hold in the textile and clothing arena since several millennia. Besides its extensive history of application in textile field and surgical sutures, recently it has gathered wide applications as advanced biomaterials for tissues, biocompatible coatings and drug delivery, etc. due to their tough mechanical properties, biocompatibility, slow degradability, diverse morphologies and slow rate of moisture absorption.

Northeastern region of India is one of the ten bio-geographic regions of India harboring diverse varieties of flora and fauna. Diverse form of silkworm species and their food plants are also precious bio-resources of this region. Muga silkworm produced by Antheraea assamensis Helfer, is an endemic, monotypic and non-diapausing species prevailing only in northeastern region of India particularly in Assam valley. It is semi domesticated, polyphagous and multivoltine in nature having five to six generations in a year and feeds on wide range of food plants- among which som (Machilus bombycina) and soalu (Litsaea polyantha) function as the primary host plants while dighloti (Litsaea salicifolia) and mejankori (Litsaea citrata) are the secondary host plants. Muga silk fiber is considered as the ‘pride of Assam’ due to its gorgeous golden color, elegant luster, high durability and robust mechanical strength and it has got the G.I. certificate as ‘muga silk of Assam’.

The silk filament spun by the silkworm is a composite material formed by two proteins- fibroin surrounded by a cementing layer of sericin. Fibroin, the core fibrous component, is a high molecular weight polypeptide whose primary structure is rich in glycine, alanine and serine amino acids in the molar ratio 3:2:1. In the fiber, fibroin
chains are aligned along the fiber axis, held together by a close network of interchain hydrogen bonds with adjacent -(gly-ala-)n- sequences forming the well known β-sheet crystals. Sericin protein, the silk gum glueing the fibroin filaments, has the same amino acid residues as fibroin but differ in proportions. While fibroin is water-insoluble owing to its highly oriented and crystalline fibrous structure, sericin is primarily amorphous and hydrophilic in nature. This behavior makes sericin easily accessible from cocoons by boiling in aqueous solutions containing soap, alkali or organic acids. In addition to fibroin and sericin the silkworm cocoons also contain some amount of pigments, waxes and other impurities. Additionally, the cocoons of wild silkmoths are reported to possess certain depositions of micrometer sized calcium oxalate crystals on their surface.

Degumming is a key process during which sericin, the glue like protein is being totally removed and the silk fibers gain the typical shiny aspect, soft handle, and elegant drape highly appreciated by the consumers. The process of degumming involves cleavage of peptide bonds of sericin by hydrolytic methods and it is removed by solubilisation or dispersion in water. It is important to use the standardized method of degumming to remove the sericin without disturbing the core fibroin.

The present study deals with bio-degumming, demineralization, chemical grafting and pigmentation profile of muga silk fiber.

Degumming has been carried out by using kolakhar, lemon, elephant apple and under high temperature and pressure (autoclave) conditions. The results have been compared with the standard method of sodium carbonate degumming (control). Among the degumming agents, treatment with high temperature and pressure resulted in highest degumming loss percent (23.67%) compared to sodium carbonate degumming (22.50%) followed by kolakhar (22.44%) and lemon (22.07%). However lowest amount of sericin loss percent (16.90%) was found in degumming with elephant apple.

The optimum pH of the degumming solutions of lemon, kolakhar and elephant apple were found to be 2.5, 10.5 and 4.5, respectively and the optimum treatment time
was recorded to be 30 min for degumming with lemon and kolakhar, whereas for elephant apple the optimum time was found to be 72 hours.

Degumming under high temperature and pressure resulted in reeling of 280 m of fiber followed by lemon (275 m) and kolakhar (260 m). Degumming with sodium carbonate produced less amount of fiber length (235 m) compared to lemon, kolakhar and autoclave degumming. Reeling of cocoons degummed with elephant apple was quite low (220 m).

In comparison to sodium carbonate degummed fibers, autoclave degummed and bio-degummed fibers exhibited greater value of tenacity, strain percent, Young’s modulus and toughness. The surface morphology of autoclave and bio-degummed fibers (kolakhar and lemon) showed smooth, uniform and clean surface of the individual fibroin brins having characteristic longitudinal striations with no sign of damage/deterioration to the silk fibroin surface.

The FTIR spectrographs showed that the native chemical structures of the silk fibers were not affected after degumming and the silk fibers retained their characteristic amide bonds. It was observed that degumming with different agents did not cause any remarkable effect on the bulk thermal properties of muga fiber.

Demineralization of the mineral layer from the surface of muga cocoons have been tried using various chemical and natural agents like ethylenediaminetetraacetic acid (EDTA), potassium carbonate, citric acid, kolakhar and lemon respectively. It is observed that both the natural and chemical agents carefully removes the mineral deposition, leaving the gummy sericin substantially intact, preventing entanglement of fibroin brins and permitting smooth wet reeling.

The removal of granular minerals from the silk was evidenced by scanning electron morphology and FTIR of demineralized cocoon fiber. The EDX spectra of the demineralized cocoon fiber confirmed the removal of calcium oxalates crystals from the fiber surface. Further, the tensile strength of demineralized and demineralized cum
degummed fibers showed superiority in contrast to sodium carbonate degummed fiber. The atomic absorption spectrometry of the demineralized solutions also confirmed the removal of calcium oxalate.

Under the implemented experimental conditions kolakhar functioned as the most efficient demineralizing agent amongst all. Demineralization with kolakhar gave the best results in producing about 350 m of fibers with very less number of fiber breaks (4). The results signify great improvement over conventional sodium carbonate degumming, which produces short discontinuous fiber lengths (235 m) with a large number of fiber breaks (30).

Grafting of BSA and casein independently onto muga silk promisingly ensued in enhancement of strength and stability to the fibers. The optimum concentration for copolymerization was found to be $1.4 \times 10^{19}$ M and $7.5 \times 10^{-3}$ M along with temperature 50 and 60 °C for BSA and casein, respectively, with the average reaction time of 4 hours for both.

FTIR studies confirm the chemical binding of the proteins onto muga fibers through shifting of the major amide bonds, accredited to grafting. Scanning electron microscopy imaging reveals rugged morphology of the grafted fibers, due to the imprints of granular proteins. Tensile strength of the fibers increases with the augmentation in grafting percent. The grafted fibers showed no loss in weight after chemical resistance measurement indicating stable bond formation between the proteins and the fibers. Moreover, the water retention capacity and dynamic contact angle study of grafted fibers suggest better hydrophobicity. The TGA and DSC analysis showed that grafting has resulted in no significant change in the inherent thermal properties of the silk fibers. The X-ray diffractograms revealed the characteristic β-sheet oriented crystalline network of silk fibroin.

Silkworms like *Antheraea yamamai, Antheraea assamensis, Philosamia ricini* and some species of *Bombyx mori* are evidenced to possess certain pigments in their cocoons. These pigments are reported to be obtained from their host plants. The color of the cocoons clearly depends on the type of host plants consumed by the silkworm. Till
now no report is available on the pigments of muga silk fiber. Methanol extracts were prepared from the muga silk cocoons and som plant leaves and a series of experiments were carried out.

The UV-visible spectroscopy of muga cocoon extract showed two major peaks at 285 and 230 nm respectively, which can be attributed to the peptide bonds and aromatic compounds like tryptophan, tyrosine and phenylalanine present in silk protein. Similarly, the UV spectra of som leaf extract showed peaks at 273 and 230 nm, which resembles the peak of cocoon fiber. While the peaks at 420 and 666 nm of som leaf can be confirmed due to the presence of chlorophyll compounds. Results of TLC and column chromatography showed separation of a single distinct compound from both the extracts with matching Rf values.

The GC-MS analysis of the purified fraction of muga silk cocoons and som leaves showed the presence of methyl isoeugenol and isoeugenyl acetate respectively. The purified fraction of cocoon fiber further analyzed by NMR spectroscopy confirmed the presence of methyl isoeugenol. It may be assumed that the isoeugenyl acetate of som plant might be converted to methyl isoeugenol during the course of metabolism in the larval growth of the silkworm. But the pathway for their conversion and the role of specific enzymes in this process is still unknown and needs further investigation. However, the presence of methyl isoeugenol in muga silk cocoon is the first report evolved from this study. Methyl isoeugenol itself is a yellow colored compound, which resembles the color of the muga cocoon and might be responsible for coloration of the same. It is a humble submission to conclude that the pigmentation profile needs further investigation in details, which could not be possible in this study. However, the study opens up many clues for further researches.