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CHEMICAL COMPOSITION, STRUCTURE, AND PROPERTIES OF NATURAL SILK: A COMPREHENSIVE REVIEW

Babadjanova Dono Davronbekovna

Asia International University

Abstract: Natural silk is a high-performance biopolymer fiber produced by *Bombyx mori* silkworms and various spider species. It is composed primarily of two proteins—fibroin and sericin—which endow silk with its unique combination of mechanical strength, biocompatibility, and biodegradability. This article reviews the chemical composition, molecular architecture, and physicochemical properties of silk, with emphasis on the crystalline beta-sheet domains of fibroin, the role of sericin as a protective coating, and the hydrogen-bonding network that governs fiber performance. Thermal stability, solubility behavior, and response to chemical treatments are discussed in detail. The article also surveys current chemical modification strategies, including degumming, fibroin dissolution, and regeneration protocols. Understanding silk chemistry at the molecular level is critical for expanding its applications in biomedicine, textile engineering, and functional materials. This review synthesizes findings from eight primary research sources to provide a rigorous chemical perspective on this remarkable natural polymer.

Keywords: silk fibroin, sericin, beta-sheet conformation, protein chemistry, biopolymer, Bombyx mori, chemical modification, silk chemistry

1. INTRODUCTION

Silk is one of the oldest and most revered natural fibers known to humanity, with documented use spanning over 5,000 years. Unlike synthetic polymers, silk originates as a protein-based biopolymer secreted by arthropods—most notably the domestic silkworm *Bombyx mori*—through a process of liquid crystalline spinning that produces a fiber of exceptional structural regularity [1]. From a chemical standpoint, silk represents a fascinating model system for studying protein self-assembly, secondary structure formation, and the relationship between molecular architecture and macroscopic mechanical performance.

The chemical study of silk has intensified in recent decades, driven by growing interest in silk-based biomaterials for tissue engineering, drug delivery, and regenerative medicine [2]. The two principal protein components—fibroin and sericin—possess markedly different amino acid compositions, solubility profiles, and functional roles. Fibroin constitutes the structural core of the fiber and is responsible for its tensile strength, while sericin acts as a glue-like binder that cements fibroin filaments together [3].

Understanding the precise chemistry of silk requires examination at multiple length scales: from the primary amino acid sequence, through secondary structural motifs such as beta-sheets and random coils, to the hierarchical fiber organization that ultimately governs bulk properties. This review consolidates current chemical knowledge of silk structure, composition, and modification, drawing on eight primary research sources to construct a coherent picture of silk from a chemistry perspective.

The objectives of this review are: (i) to describe the chemical composition and amino acid profile of silk fibroin and sericin; (ii) to analyze the secondary and tertiary structural features that define silk's mechanical behavior; (iii) to examine the physicochemical properties including thermal stability and solubility; and (iv) to survey key chemical processing strategies used to regenerate and modify silk for advanced applications.

2. MATERIALS AND METHODS

This review was conducted as a systematic literature analysis of peer-reviewed research on the chemistry of natural silk. A comprehensive database search was performed across Web of Science, Scopus, and PubMed using the search terms: "silk fibroin chemistry," "sericin composition," "silk beta-sheet structure," "silk thermal properties," and "silk chemical modification." Studies were included if they reported original experimental data on the chemical characterization of silk derived from *Bombyx mori* or comparable sources, and were published in high-impact peer-reviewed journals.

Eight primary sources were selected based on their methodological rigor, relevance to the chemical aspects of silk, and citation impact. Data on amino acid composition were extracted from biochemical characterization studies employing amino acid analysis, nuclear magnetic resonance (NMR) spectroscopy, and Fourier transform infrared spectroscopy (FTIR). Structural data were derived from X-ray diffraction (XRD), solid-state NMR, and transmission electron microscopy (TEM) studies [4].

Thermal properties were compared across studies utilizing thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Chemical modification data were gathered from experimental studies investigating ionic liquid dissolution, LiBr-mediated solubilization, and enzymatic degumming. All data were evaluated for internal consistency, and where discrepancies existed across sources, the most methodologically comprehensive study was prioritized.

To ensure reproducibility and transparency, all quantitative data cited in this review are attributed to their original source. Amino acid percentages, crystallinity indices, and thermal decomposition temperatures are presented as reported in the primary literature, with units and experimental conditions preserved. No new experimental data were generated for this review.

3. RESULTS

3.1 Chemical Composition of Silk Fibroin

Silk fibroin is a fibrous protein characterized by a highly repetitive primary sequence dominated by glycine (Gly), alanine (Ala), and serine (Ser), which together account for approximately 85–90% of total residues [1]. The canonical repeating hexapeptide unit (Gly-Ala-Gly-Ala-Gly-Ser) is responsible for the formation of antiparallel beta-sheet crystallites that provide fibroin with its remarkable tensile strength. Glycine, comprising roughly 43–46 mol% of fibroin, occupies every second position in the crystalline regions due to the spatial constraints of beta-sheet packing, where its minimal side chain (a single hydrogen atom) is essential for tight interchain stacking [1].

Alanine (approximately 28–30 mol%) provides the hydrophobic methyl groups that face alternating sides of the beta-sheet lamellae, contributing to the van der Waals stabilization of the crystalline domains [5]. Serine (approximately 12 mol%) introduces hydroxyl functionality that participates in hydrogen bonding and is also a site for potential chemical derivatization. Minor residues including tyrosine, valine, and threonine are predominantly located in the amorphous regions and contribute to conformational flexibility. The molecular weight of the heavy chain of fibroin ranges from 325 to 390 kDa, and it is disulfide-linked to a light chain (~26 kDa) and associated with a glycoprotein P25 (~25 kDa) that facilitates secretion [2].

3.2 Sericin Chemistry and Composition

Sericin is a hydrophilic, globular protein that envelops the fibroin core and accounts for 20–30% of the total mass of raw silk [3]. Its amino acid composition is markedly different from fibroin, being rich in serine (~33 mol%), aspartic acid (~16 mol%), and glycine (~14 mol%). The high serine content, with its pendant hydroxyl groups, makes sericin highly hygroscopic and readily soluble in hot water. Sericin exists in multiple isoforms (sericin-A, sericin-B, and sericin-C) encoded by a single gene through alternative splicing, resulting in molecular weights ranging from approximately 150 to 400 kDa [3].

FTIR spectroscopy of sericin reveals characteristic amide I absorption at ~1630 cm^{-1} and amide II at ~1525 cm^{-1}, consistent with a predominantly random coil and beta-turn secondary structure in the hydrated state [6]. Upon drying, sericin undergoes a conformational transition toward beta-sheet structure, which reduces its solubility. The removal of sericin—referred to as degumming—is a critical chemical processing step that typically involves boiling raw silk in an alkaline soap solution or dilute sodium carbonate, releasing fibroin filaments for textile or biomedical applications.

3.3 Secondary Structure and Crystallinity

X-ray diffraction studies of degummed *B. mori* silk fiber reveal a silk II crystal structure characterized by antiparallel beta-sheets stacked along the b-axis with a periodicity of approximately 9.3 Å [4]. The unit cell of silk II contains four glycine-alanine dipeptide units, with hydrogen bonds forming along the chain direction and hydrophobic interactions stabilizing the stacking of adjacent sheets. Crystallinity index values typically range from 35 to 60%, depending on the reeling conditions and post-treatment history of the fiber [4].

Solid-state ^{13}C NMR spectroscopy has been instrumental in quantifying the relative proportions of silk I (pre-spinning, water-soluble form with predominantly alpha-helical and random coil conformations) and silk II (final fiber, beta-sheet dominant) [7]. The Cβ chemical shift of alanine is a particularly reliable conformational probe: resonances at ~16 ppm indicate beta-sheet, while shifts near ~14 ppm indicate helical or random coil conformations. The irreversible silk I to silk II transition is driven by mechanical shear, pH drop, and ion exchange occurring in the spinning duct of the silkworm, and can be replicated in vitro by stretching, alcohol treatment, or sonication of regenerated fibroin solutions.

3.4 Thermal and Physicochemical Properties

Thermogravimetric analysis of native silk fiber shows an initial mass loss of 2–5% below 100 °C attributed to moisture desorption, followed by a major thermal decomposition event commencing at approximately 270–290 °C and peaking near 320 °C, corresponding to peptide bond cleavage and side-chain degradation [5]. DSC thermograms exhibit an endothermic peak at ~175 °C assigned to crystalline melting of the beta-sheet domains, overlapping with the onset of chemical decomposition, which precludes melt processing of silk under standard conditions.

The solubility of native silk fibroin in water is negligible owing to the high degree of crystallinity and extensive intermolecular hydrogen bonding. Dissolution requires chaotropic salts such as lithium bromide (LiBr, 9.3 M), lithium thiocyanate, or ionic liquids such as 1-butyl-3-methylimidazolium chloride [8]. In the LiBr dissolution process, lithium cations coordinate to carbonyl oxygens of the peptide backbone while bromide anions disrupt N-H···O=C hydrogen bonds, leading to chain unfolding and dissolution. Subsequent dialysis against water removes the salt and yields a regenerated fibroin solution (typically 2–8 wt%) that can be processed into films, sponges, hydrogels, or electrospun fibers [8].

3.5 Chemical Modification Strategies

The functional groups present on silk—hydroxyl (Ser, Thr, Tyr), amine (Lys), carboxyl (Asp, Glu), and phenol (Tyr)—offer multiple handles for chemical derivatization. Tyrosine residues have been exploited for diazonium coupling reactions to introduce chromophoric groups, and for horseradish peroxidase-catalyzed crosslinking to form stable hydrogels without cytotoxic crosslinkers [6]. Hydroxyl groups on serine and threonine can be esterified or phosphorylated, while amine groups on lysine react readily with N-hydroxysuccinimide (NHS) esters for bioconjugation.

Graft copolymerization of acrylic monomers onto silk fibroin, initiated by cerium(IV) ammonium nitrate or by gamma-irradiation, has been reported to improve dyeability, flame retardancy, and moisture management [7]. These reactions proceed primarily at serine and glycine residues in the amorphous regions of the fiber, as the crystalline beta-sheet domains are inaccessible to reagents under mild conditions. The degree of modification, typically quantified by gravimetric add-on or FTIR ratio analysis, is thus closely linked to the crystallinity index of the substrate fiber.

4. DISCUSSION

The chemical architecture of silk fibroin—a near-perfect alternation of glycine with bulkier residues in the crystalline core—represents an evolutionary optimization for fiber formation. The minimal steric profile of glycine and the complementary hydrophobicity of alanine generate an ideal building block for tightly packed antiparallel beta-sheets, a motif that delivers high tensile modulus (~10–15 GPa) and breaking stress (~500–700 MPa) at low density [1, 4]. This performance places silk among the strongest naturally occurring materials, rivaling many synthetic polymers.

The dichotomy between the crystalline fibroin core and the amorphous sericin sheath is chemically instructive. Sericin's high serine content and predominantly coil conformation make it soluble and easily removed, while fibroin's regular beta-sheet domains are kinetically trapped in an insoluble state under ambient conditions [3]. This architectural separation of function—load-bearing versus adhesive—is analogous to composite material design principles and highlights the sophistication of biological polymer engineering.

From a processing chemistry standpoint, the irreversibility of the silk I to silk II transition is both a challenge and an opportunity. Once formed, the beta-sheet crystallites resist dissolution and thermal processing, limiting conventional polymer fabrication routes. However, the LiBr dissolution–dialysis–regeneration cycle effectively deconstructs the fiber into its soluble precursor state, permitting reprocessing into diverse morphologies [8]. The fidelity of secondary structure recovery during regeneration—quantifiable by FTIR and NMR—is a key determinant of the mechanical properties of regenerated materials and remains an active research focus.

The thermal decomposition behavior of silk, with its relatively low onset temperature (~270 °C) compared to synthetic polyamides (>350 °C), reflects the susceptibility of peptide bonds to pyrolytic cleavage and the limited thermodynamic stability of hydrogen-bonded beta-sheets at elevated temperatures [5]. This property has practical implications for textile finishing operations (dyeing, steaming) and for biomedical sterilization protocols, where autoclaving

(121 °C, wet heat) is tolerated but dry heat sterilization at temperatures above 160 °C is destructive.

Chemical modification of silk expands its functional versatility beyond its native properties. The selective reactivity of tyrosine residues under mild oxidative conditions has been particularly valuable for crosslinking-based gelation without exogenous toxic reagents, a significant advantage for cell-encapsulation applications [6]. Graft copolymerization approaches, while effective for property enhancement, must be carefully controlled to preserve the structural integrity of the fibroin crystalline domains and avoid excessive chain scission [7].

Future directions in silk chemistry include the development of green solvent systems for fibroin dissolution to replace chaotropic salts, the design of stimuli-responsive silk-based hydrogels for controlled drug release, and the integration of silk with inorganic nanoparticles for catalytic and electronic applications. The intrinsic biocompatibility, tunable degradation, and rich chemistry of silk position it as a compelling platform material for next-generation functional biomaterials [2].

5. CONCLUSION

This review has demonstrated that natural silk is a chemically sophisticated biopolymer whose properties emerge from a hierarchical interplay of amino acid composition, secondary structure formation, and supramolecular organization. The dominance of glycine, alanine, and serine in fibroin's crystalline beta-sheet regions underpins the fiber's exceptional tensile performance, while sericin's serine-rich, hydrophilic chemistry serves an adhesive and protective function. Thermal analysis reveals moderate decomposition temperatures that constrain processing options, while the LiBr dissolution system provides a well-characterized pathway for regenerated fibroin fabrication.

Chemical modification of silk through tyrosine coupling, amine bioconjugation, and graft copolymerization offers diverse routes to functional materials, with reaction selectivity dictated by the accessibility of residues in amorphous versus crystalline domains. Collectively, the chemistry of silk presents both fundamental insights into protein fiber formation and practical strategies for engineering advanced materials. Continued interdisciplinary research combining protein chemistry, materials science, and bioengineering will be essential to fully realize the potential of silk as a platform for sustainable, high-performance materials.

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