

## Review Article

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# Textile chemistry of sericulture: molecular insights, processing and applications



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## ABSTRACT

Sericulture integrates biology and textile chemistry, with silk fibroin and sericin forming the foundation of its structural and functional properties. Fibroin, a block-copolymer-like protein, achieves exceptional mechanical strength, elasticity, and luster through the balance of crystalline  $\beta$ -sheet domains and amorphous regions. Sericin, the hydrophilic coating protein, exhibits diverse bioactivities including antioxidant, antimicrobial, and wound-healing potential, making it valuable for biomedical and cosmetic industries. Chemical processes such as degumming, dyeing and finishing significantly influence fiber quality, structural integrity, and sustainability. Traditional soap-alkali methods risk fiber degradation, while enzymatic and eco-friendly approaches better preserve fibroin properties. Conventional soap-alkali degumming leads to partial fibroin degradation and high environmental pollution, while achieving uniform, durable dye fixation on silk remains difficult due to weak molecular interactions and limited fastness. The large-scale adoption of enzymatic and microbial processing is still restricted by cost, enzyme stability, and industrial scalability. Advances in dye-fiber interactions, natural dye applications and functional finishing (UV-protective, antimicrobial, hydrophobic) expand the versatility of silk textiles. Analytical tools, including spectroscopy, microscopy, and thermal analysis, provide insights into hierarchical structures and performance. This synthesis of molecular chemistry and processing highlights silk's dual role as a luxury textile and an innovative biomaterial for future applications.

**Keywords:** Silk fibroin, Sericin, Sericin Bioactivity, Degumming, Dyeing chemistry, Functional finishing, Biocompatibility, Textile applications, Natural dyes, Bioactivity, Eco-Friendly degumming, Enzymatic processing and Biomaterials.

## 1. Introduction

Silk fibroin, the structural protein of *Bombyx mori* silk, derives its unique properties from its amino acid composition and hierarchical organization of secondary structures. Together, these molecular characteristics explain the exceptional mechanical and functional performance of silk fibers. The fibroin polypeptide is primarily composed of repetitive sequences rich in glycine (Gly) and alanine (Ala), which dominate the crystalline domains. These residues align in anti-parallel arrangements, stabilized by intermolecular hydrogen bonds, and form highly ordered  $\beta$ -sheet crystallites [28]. Acting as rigid, hydrophobic blocks, these crystallites are responsible for the high tensile strength and stiffness of silk. In contrast, the amorphous domains of fibroin consist of irregular sequences containing amino acids such as serine, tyrosine, and valine. These regions are relatively disordered, hydrophilic, and moisture-retentive, functioning as a soft matrix surrounding the crystalline blocks [90]. The balance between crystalline and amorphous phases imparts silk with its signature combination of strength, elasticity, and toughness (Table 1).

Thus, fibroin can be described as a block copolymer-like system, where alternating crystalline (Gly-Ala-rich  $\beta$ -sheets) and amorphous segments form a hierarchical structure. This molecular architecture underpins the superior mechanical, chemical, and biological performance of silk compared with most natural and synthetic polymers [79].

### Role in Mechanical Strength

- Crystalline structures:** The  $\beta$ -sheet crystallites provide high tensile strength and stiffness [28].
- Amorphous regions:** These domains impart elasticity, allowing silk to deform and absorb energy without breaking [90].
- High strength-to-density ratio:** The interplay of crystalline and amorphous structures yields excellent mechanical efficiency relative to its low density, positioning silk as an advanced material for load-bearing uses [88].
- Biocompatibility:** Beyond mechanics, silk fibroin offers high biocompatibility and controllable degradation rates, making it a preferred biomaterial for sutures, scaffolds, and wound dressings [80].

### Role in Luster

- Triangular cross-section:** Silk's distinctive luster arises from its roughly triangular fiber cross-section, which refracts light at varying angles [90].

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- **Light reflection:** Acting like a prism, the triangular structure creates silk's signature sheen and sparkle.
- **Surface smoothness:** The fine, smooth surface of silk fibers enhances reflection and contributes to their characteristic brilliance.

**Table 1. Molecular composition and structural organization of silk fibroin**

Component	Amino acid composition	Structural feature	Functional contribution
Crystalline domains	Rich in glycine (Gly) and alanine (Ala)	Anti-parallel $\beta$ -sheets	High tensile strength, stiffness
Amorphous domains	Contain serine, tyrosine, valine	Disordered hydrophilic matrix	Elasticity, toughness, moisture absorption
Overall fibroin	Block-copolymer-like structure	Alternating crystalline and amorphous regions	Combination of strength, ductility, biocompatibility

## 2. Chemistry of Sericin

Sericin, a protein derived from silk, functions as an adhesive material by binding the two fibroin filaments together [70]. It is a globular protein primarily composed of random coil structures and  $\beta$ -sheets, and its conformation is strongly influenced by environmental conditions. The transformation from random coil to  $\beta$ -sheet configurations is promoted by changes in temperature, humidity, and mechanical stress. Sericin remains soluble in water at temperatures above 50 °C [71], but at lower temperatures, its solubility decreases progressively. [71] investigated the role of poloxamer, a polymeric surfactant, on sericin gelation and reported that its addition accelerated the transition from random coil to  $\beta$ -sheet structures. They further observed that gelation occurred more rapidly at higher sericin concentrations and elevated temperatures. Similarly, [125] demonstrated through chromatographic analysis that sericin is water-soluble within the silk gland but loses solubility after spinning and drying due to  $\beta$ -sheet formation, which renders it less soluble compared with its amorphous state.

Chemically, sericin is a highly hydrophilic protein enriched with hydroxyl, carboxyl, and other polar functional groups. While serine is its predominant amino acid, sericin contains 17 additional amino acids. This diverse amino acid composition gives rise to three structural variants-SER-1, SER-2, and SER-3-each with distinct amino acid profiles and molecular weight ranges [32].

The biosynthesis of sericin occurs within the silk gland of *Bombyx mori*. The gland is divided into three specialized regions: the anterior silk gland (ASG), which acts as an excretory duct; the middle silk gland (MSG), responsible for the production and secretion of the three sericin fractions; and the posterior silk gland (PSG), which secretes fibroin [70].

## Biophysical Characteristics

Sericin has emerged as a multifunctional biomaterial with properties that support applications across diverse domains. Its most notable feature is biocompatibility, defined as the ability of a material to interact with living tissues without provoking adverse immune responses. Sericin elicits minimal immunological reactions when in contact with biological systems, thereby reducing risks of inflammation or rejection [58, 136]. This makes it particularly suitable for wound healing, tissue engineering, and drug delivery systems [117].

Sericin can be naturally decomposed by proteolytic enzymes such as proteases, which hydrolyze peptide bonds into smaller peptides and amino acids [55]. While this aligns well with sustainable biomedical practices, the long-term impact of sericin degradation by-products remains underexplored. Recent work highlights the need to evaluate potential interactions of these by-products with endogenous biomolecules to confirm their safety and therapeutic viability [1].

In addition to biocompatibility and biodegradability, sericin exhibits a range of bioactive properties.

These include anti-inflammatory, antibacterial, antioxidant and UV-protective effects, which extend its applications into skincare, regenerative medicine, food packaging and functional textiles. The anti-inflammatory properties of sericin are associated with its ability to modulate cytokine release, particularly interleukin-1 (IL-1) and tumour necrosis factor-alpha (TNF- $\alpha$ ), which are central mediators of inflammatory responses [117, 2].

Its antibacterial activity is linked to cysteine residues. The sulphydryl groups in cysteine form weak hydrogen bonds with oxygen or nitrogen atoms, producing reactive intermediates that interfere with microbial enzymatic and metabolic pathways, thereby suppressing bacterial survival [117]. Sericin also demonstrates strong antioxidant activity, largely due to its high content of serine and threonine residues, which can chelate transition metals such as copper and iron, preventing the catalytic generation of reactive oxygen species (ROS) [86]. These antioxidant effects not only counteract oxidative stress but also contribute to sericin's anti-aging potential by delaying skin aging [68]. Furthermore, amino acids such as arginine and alanine enhance its anti-tyrosinase activity, an attribute relevant for cosmetic and dermatological applications [136]. Taken together, the chemical diversity, structural adaptability, and multifunctional bioactivities of sericin make it a promising biomaterial with applications extending from biomedical devices to sustainable textiles.

## Functional Applications of Sericin in Biomedical and Cosmetic Industries

### Biomedical Industry

Silk sericin, a natural protein derived from the cocoon of *Bombyx mori*, has attracted significant attention in biomedical research due to its biocompatibility, biodegradability, hydrophilicity and pharmacological properties [95]. Its diverse bioactivities make it a promising candidate for therapeutic, regenerative and preventive applications.

### 1. Anticancer Activity

Sericin exhibits anticancer potential through its antioxidant and pro-apoptotic effects. It reduces oxidative stress in tissues, suppresses the proliferation of melanoma and colon cancer cells and promotes apoptosis, thereby hindering tumour progression [146, 122]. In vivo experiments on rats confirmed that sericin administration effectively limited tumour growth and enhanced cancer cell death, highlighting its role as a natural adjunct in cancer prevention and therapy.

### 2. Wound Healing and Tissue Regeneration

Sericin enhances wound repair by stimulating fibroblast and keratinocyte proliferation, promoting collagen deposition, and reducing inflammation. Clinical studies reported that sericin-based creams accelerated epithelialization, reducing recovery time from 15 to 11 days compared to controls [4]. Additionally, sericin hydrogels and composite biomaterials have shown efficacy in supporting connective tissue and epithelial

regeneration, making them suitable for advanced wound dressings and skin substitutes [77].

### 3. Immunomodulatory Effects

Sericin also demonstrates immunoregulatory functions. Dietary supplementation in animal models reduced inflammatory markers such as CD8a and CD80 without systemic side effects [64]. Moreover, sericin-derived oligopeptides enhanced natural killer (NK) cell activity and stimulated cytokine production, including interleukin-2 (IL-2) and interferon-alpha (IFN- $\alpha$ ), strengthening immune defense mechanisms.

### 4. Anticoagulant Properties

Sulfated derivatives of sericin display anticoagulant activity comparable to heparin. When serine residues were chemically sulfated, sericin significantly inhibited coagulation pathways without interfering with fibrinolysis or polymerization [112]. This positions sericin as a potential biocompatible alternative to synthetic anticoagulants in thrombosis therapy.

### 5. Antioxidant Properties

Sericin possesses strong antioxidant capacity, confirmed through assays such as DPPH radical scavenging, lipid peroxidation inhibition, and ORAC analysis. By neutralizing reactive oxygen species (ROS), sericin protects biomolecules from oxidative stress [126]. This antioxidant mechanism underpins its cardioprotective, anticancer, and wound-healing effects [77].

### 6. Cardioprotective Effects

Sericin also demonstrates cardioprotective effects by reducing oxidative damage and improving cardiac resilience. Animal studies showed that sericin extracts reduced myocardial infarction severity and offered protection against doxorubicin-induced cardiotoxicity [122]. These effects are attributed to its antioxidant amino acids and flavonoids, which act as free radical scavengers.

### Cosmetic Industry

Beyond biomedical uses, sericin is widely recognized in the cosmetic industry due to its hydrophilicity, skin compatibility, antioxidant properties, and amino acid composition, which closely resembles the natural moisturizing factor (NMF) of human skin [1]. Its high serine content (~30%) makes it an excellent humectant and elasticity enhancer. Unlike glycerol, which can clog pores at high concentrations, sericin's relatively low molecular weight enables deep absorption and long-lasting hydration [115].

### Moisturizing and Anti-Aging Applications

Sericin exhibits superior moisturizing efficacy, with a 3% sericin solution showing comparable hygroscopicity to 60% glycerol [115]. Dietary supplementation with 1% sericin also improved skin hydration over a 10-week period by enhancing filaggrin and free amino acid levels, demonstrating both topical and dietary benefits for skin elasticity and wrinkle reduction [65].

### Skin Whitening and Pigmentation Control

Sericin functions as a natural skin-whitening agent by inhibiting tyrosinase, a key enzyme in melanin biosynthesis. At just 1% concentration, sericin reduced tyrosinase activity by more than 50%, leading to decreased melanin production and visible whitening effects [115, 138]. This positions it as a safer alternative to synthetic depigmenting agents.

### Hair and Nail Care

Due to its strong binding affinity with keratin, sericin enhances hair elasticity, strength, and gloss [115]. In nail care, sericin formulations (0.02-20%) have been patented for preventing brittleness and improving nail smoothness and shine [116].

### Cosmetic Textile Finishing

Sericin has also been integrated into cosmetic textiles. A sericin/ $\beta$ -cyclodextrin finish applied to cotton fabrics demonstrated antioxidant activity, UV protection, and improved moisture transmission, highlighting its potential in dermo-cosmetic fabrics [118].

### Industrial Relevance

With its multifunctional benefits, sericin is incorporated into moisturizers, whitening creams, shampoos, conditioners, and cosmetic textiles. The global sericin market is projected to reach USD 537.6 million by 2032, reflecting its growing demand in personal care and pharmaceuticals [39].

## 2.3 Variations Across Silk Types

### Comparative Chemical and Physical Properties of Mulberry and Non-Mulberry Silks

The properties of silk vary significantly depending on whether it is produced by *Bombyx mori* (mulberry silk) or by non-mulberry species such as tasar, eri, and muga silkworms. These differences in chemical composition and physical performance determine the suitability of each silk type for specific applications in textiles, biomaterials, and industrial products [121].

### Chemical Properties

Mulberry silk is characterized by its fineness (2.1 dtex) and superior acid resistance, whereas tasar silk is coarser (8.9 dtex) with moderate acid resistance. Eri silk fibers (3.09 dtex) and muga silk (4.2 dtex) also exhibit good acid resistance. In terms of cocoon weight, mulberry cocoons are significantly lighter (1.55 g) compared to tasar (16.39 g), eri (3.23 g) and muga (4.5-8.55 g). Elongation at break varies widely: mulberry (9.34-12.99%), tasar (21%), eri (16.88-22.6%), and muga (8.91%). Despite these differences, all silk types are destroyed by bleaching and dissolve in alkali. Cross-sectional morphology further distinguishes them: mulberry silk has a triangular cross-section, while tasar, eri and muga silks typically display elongated triangular or needle-like shapes [121].

### Physical Properties

In terms of physical performance, mulberry silk filaments are longer (869.17-1424 m) compared with tasar (750 m), eri (317.8-452.37 m), and muga (600-800 m). The density of mulberry and tasar silk is similar (1.3525 g/cm<sup>3</sup>), slightly higher than eri (1.303 g/cm<sup>3</sup>) and muga (1.307 g/cm<sup>3</sup>). Tensile strength varies greatly: tasar (28.6 cN) far exceeds mulberry (7.17-12.85 cN), eri (3.27-5.16 cN), and muga (3.7 cN). Fiber toughness is also highest in muga (1.1 gf/den), followed by tasar (0.9 gf/den), mulberry (0.6 gf/den), and eri (0.5 gf/den). Moisture absorption ranges from 8% (muga) to 10.76% (tasar), with mulberry and eri absorbing 9% and 10% respectively. Visually, mulberry silk appears smooth with a gray-yellow hue, tasar is brown and harsh in texture, eri is irregular and gray but smooth to touch, while muga is golden yellow and comparatively coarse [121].

### 3. Pre-Processing Chemistry of Silk

#### Degumming of Silk

Degumming is a critical process in silk production, involving the removal of sericin to obtain pure fibroin fibers. The method selected—whether soap-alkali, enzymatic, or eco-friendly—directly influences fiber chemistry, structural integrity, and environmental sustainability [47].

#### Silk Degumming Chemistry

Degumming works by hydrolyzing and removing sericin, the proteinaceous coating that surrounds fibroin filaments, through either chemical or enzymatic action. During the process, peptide or glycosidic bonds in sericin are cleaved, enabling its detachment and yielding lustrous, smooth fibroin fibers. Traditionally, agents such as soap, sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) or proteases are used, with solution pH and temperature playing key roles in determining degumming efficiency and fiber integrity [132]. Comparative evaluations confirm that the choice of method greatly affects fiber performance [29].

#### Soap-Alkali Degumming

Soap-alkali degumming employs soap (typically sodium stearate, an anionic surfactant) and sodium carbonate. Soap hydrolysis under alkaline conditions generates sodium ions that emulsify and separate sericin from fibroin. This method can remove 60-80% of sericin within 20-25 minutes, depending on concentration and treatment duration. However, excessively strong conditions may lead to partial fibroin degradation, loss of tensile strength, or reduced colour intensity [132].

#### Enzymatic and Eco-Friendly Degumming

Enzymatic degumming represents a gentler alternative, employing proteases sourced from bacteria, plants, or commercial blends, often combined with mild detergents. Enzymes such as trypsin, papain, and bacterial proteases selectively hydrolyze sericin while sparing fibroin. This reduces chemical consumption, energy use, and effluent pollution, while preserving fiber smoothness and strength [37, 97].

Emerging eco-friendly methods include microbial biodegumming, plant-derived enzymes [27], and even genetic engineering of silkworms to produce self-degumming cocoons. Wang et al. [137] demonstrated that genetically engineered silkworms capable of self-degumming significantly reduced process steps and environmental impact, while maintaining fiber quality. Enzymatic approaches achieve degumming efficiencies up to 87%, yielding higher-quality fibroin with smoother surfaces compared to conventional methods [147].

#### Effect on Fibroin Integrity and Fiber Properties

The choice of degumming method has profound effects on fibroin integrity. Strong alkaline treatments, particularly under prolonged exposure, may cause partial hydrolysis of fibroin polypeptides, reducing tensile strength, crystallinity, and thermal stability [14]. In contrast, enzymatic and eco-friendly methods, operating under mild conditions, better preserve fibroin's natural structure. Comparative analyses using SEM, FTIR, and tensile testing confirm that enzymatically degummed fibers exhibit smoother surfaces, higher luster, and minimal structural damage [23, 147].

Overall, eco-friendly and enzymatic approaches align more closely with sustainable textile practices, offering an environmentally conscious alternative to conventional soap-alkali methods while maintaining fiber performance [97, 137].

### 4. Dyeing and Finishing Chemistry

Dyeing is a fundamental finishing process in textile manufacturing, involving the transfer of colorants to fibers under controlled physicochemical conditions to achieve durable coloration. The chemistry of dyeing is primarily dictated by the interactions between dye molecules and functional groups of fiber polymers. Four key types of molecular forces—ionic bonds, hydrogen bonds, van der Waals interactions, and covalent bonds—govern dye-fiber affinity and influence the fastness of dyed fabrics [114].

#### Mechanisms of Dye-Fiber Interactions

Ionic interactions play a central role in binding dyes to protein fibers such as silk and wool, which contain amino and carboxyl groups along their polypeptide backbones. Acid dyes, for instance, attach to wool by forming salt-type linkages between negatively charged dye sulfonate groups and protonated amino groups of the fiber. While these bonds are relatively weak and may limit wash fastness, they remain crucial for effective coloration. Conversely, basic dyes interact with negatively charged groups in silk, wool, and acrylic fibers, with stronger fixation observed in hydrophobic substrates such as polyacrylonitrile, where water accessibility is reduced. Hydrogen bonding also contributes significantly to dye-fiber interactions. Natural fibers such as silk and wool contain carbonyl ( $\text{C}=\text{O}$ ), hydroxyl ( $-\text{OH}$ )<sub>2</sub>, and amino ( $-\text{NH}_2$ ) groups that readily form hydrogen bonds with dyes. Although individual bonds are weak, their cumulative effect stabilizes dye-fiber complexes. However, in cellulose fibers, water molecules compete for hydrogen bonding, making hydrogen bonding alone insufficient to explain dye fixation [114].

Van der Waals forces dominate interactions in hydrophobic fibers such as polyester. These weak intermolecular forces, including dipole-induced dipole and London dispersion interactions, occur between dye aromatic rings and fiber macromolecules. Their effectiveness is maximized when dye molecules are closely packed in fiber micro-voids, as seen in disperse dyeing of polyester [83].

Reactive dyeing introduces a more durable interaction mechanism by establishing covalent bonds between dye molecules and fibers. Reactive dyes such as dichloro-s-triazine derivatives undergo nucleophilic substitution with hydroxyl groups in cellulose or amino groups in silk and wool, producing stable covalent linkages that impart excellent washing fastness [114]. For instance, in dichloro-s-triazine reactive dyeing of cotton, one chlorine atom reacts with cellulose hydroxyls, while another may be substituted by water, generating a hydrolyzed dye with no affinity for the fiber [83].

#### Fiber-Dye Compatibility

These interaction mechanisms explain the fiber specificity of dyeing. Cotton is typically dyed using direct, vat, reactive, Sulphur, and azoic dyes, whereas silk and wool are suited to acid, basic, and reactive dyes. Polyester, due to its hydrophobic nature, requires disperse dyes, while polyacrylonitrile favors cationic dyes. Polypropylene, being chemically inert, can only be dyed with specialized disperse dyes [114].

#### Finishing Treatments

Post-dyeing finishing treatments such as mercerization, softening, and functional finishing (e.g., antimicrobial, UV-protective and wrinkle-resistant treatments) further enhance fabric performance.

These chemical modifications alter fiber morphology, improve dye uptake and increase colour durability. With growing demand for sustainability, plasma treatments and enzymatic modifications are increasingly being explored as eco-friendly alternatives to harsh chemical finishing [11].

### Traditional Dyeing Methods

Classical dyeing techniques were developed to exploit specific chemical affinities between dyes and fibers. Direct dyeing, vat dyeing, mordant dyeing, disperse dyeing, azoic dyeing, acid dyeing, and reactive dyeing each reflect unique combinations of solubility, fixation chemistry, and fiber compatibility [114]. Vat dyeing involves insoluble vat dyes such as indigo, which are reduced to soluble leuco forms using sodium hydrosulphite in alkaline solution. Once absorbed, they are oxidized back to insoluble forms, becoming trapped within the fiber and offering superior fastness [11].

Mordant dyeing employs metallic salts such as alum, iron, or chromium to form coordination complexes between fiber functional groups and dye molecules. These "lake" complexes yield high fastness but have declined in use due to environmental concerns [111].

Azoic dyeing, also known as naphthol dyeing, generates azo dyes in situ within fibers. Cotton impregnated with a coupling component is treated with diazonium salts to form insoluble azo pigments inside the fiber, yielding bright shades but raising health concerns due to carcinogenic amines [114].

Acid dyeing, widely used for silk, wool, and polyamides, depends on ionic interactions between sulfonic acid groups of dyes and cationic amino groups of fibers in acidic baths. This produces brilliant colours but variable wash fastness [130].

Reactive dyeing, particularly for cotton, employs reactive moieties such as dichloro-s-triazine or vinyl sulfone, which covalently bond to cellulose hydroxyls. This process offers excellent wash fastness but requires careful management of hydrolyzed, unfixed dyes to avoid environmental impacts [114].

### Natural Dyes and Mordanting Techniques

Natural dyes, used for millennia, remain valued for their eco-friendliness, non-toxicity, and biodegradability [69, 41]. They derive from plant, animal, mineral, and fungal sources, each contributing diverse colour ranges.

Plant dyes include indigo (*Indigofera tinctoria*) for blue, madder (*Rubia tinctorum*) for red, turmeric (*Curcuma longa*) for yellow-orange, and henna (*Lawsonia inermis*) for reddish-brown hues [62, 22, 49, 63]. Logwood (*Haematoxylum campechianum*), onion skins, and marigold petals also yield distinctive pigments [45, 10, 92].

Animal dyes historically included cochineal (*Dactylopius coccus*), which produces carmine red [21, 61], and Tyrian purple, extracted from Murex snails, symbolic of royalty [120, 128]. Mineral dyes such as ultramarine from lapis lazuli and ochre from iron oxides provided durable pigments in ancient art [46, 15].

Fungal pigments, such as orchil from *Roccella* spp., are gaining attention for sustainable textile coloration [51, 119]. Mordanting improves dye-fiber affinity and fastness by forming stable complexes between dyes and fibers. Common mordants include alum, tannins, iron salts, and copper salts, each modifying colour shades and fastness differently [22, 57].

### Modern Synthetic Dyes

#### The advent of synthetic dyes transformed textile coloration.

Acid dyes, anionic and water-soluble, bind to protein fibers via ionic interactions with amino groups under acidic conditions, producing bright colours with variable fastness [35, 110].

Reactive dyes contain electrophilic groups (e.g., dichlorotriazine, vinyl sulfone) that form covalent bonds with hydroxyl or amino groups in fibers, ensuring excellent wash fastness and versatility [129, 42].

Metal-complex dyes, derived from acid dyes, involve coordination of metals such as chromium or cobalt with dye ligands, yielding superior fastness on wool, silk, and nylon, though raising environmental concerns [26].

### Molecular Insights into Dye-Silk Interactions

High-resolution NMR studies demonstrate that serine and tyrosine residues in silk fibroin play pivotal roles in dye binding. Serine hydroxyls form hydrogen bonds with hydrophilic dyes, while tyrosine aromatic rings facilitate hydrophobic and  $\pi$ - $\pi$  interactions, enhancing fastness. The fibroin secondary structure (silk I or II) influences accessibility of these residues and thus dye uptake [6].

Complementary work shows that fibroin's charge characteristics and hydrophobicity modulate dye sorption. Methanol-treated fibroin films, for example, absorb more hydrophobic dyes, while electrostatic forces govern interactions between charged dyes and silk [140].

Recent adsorption studies reveal that fibroin-based microparticles strongly bind cationic dyes such as methylene blue through hydrogen bonds with lysine and ionic interactions with glutamate residues, with efficiency enhanced at higher pH values [101].

Further, H acid-containing azo dyes have been shown to covalently bond to tyrosine and other nucleophilic amino acid residues in fibroin via Mannich-type reactions, improving wet fastness and colour durability [48].

### Finishing and Functionalization

#### Softening, Anti-Crease and Anti-Yellowing Treatments

An innovative approach to prevent yellowing in silk fabrics is described in patent CN1057304A, which introduces an anti-yellowing finishing agent designed to mitigate discoloration caused by light exposure and aging. This agent contains UV absorbers (such as UV-9, UV-531, and UV-327), chlorinated paraffin wax, emulsifying agents, and bleeding agents, emulsified into water-dispersible forms for uniform application on silk textiles. The UV absorbers convert harmful UV radiation into harmless heat, thereby protecting silk fibers from photooxidative yellowing. Chlorinated paraffin wax enhances fabric softness and adhesion, while emulsifiers with optimized hydrophile-lipophile balance (HLB) improve solution stability and application. The treatment process-soaking, drying, and baking-results in silk fabrics with reduced yellowness, enhanced UV resistance, and preserved breathability and softness, offering a scalable, cost-effective and durable finishing solution.

Building on this, Li, Dong, Xing, and Chen [74] investigated 2,4,6-trichloropyrimidine (TLP) as a formaldehyde-free anti-crease finishing agent. Under optimized conditions (3 g/L TLP, 6 g/L NaHCO<sub>3</sub>, 8 g/L Na<sub>2</sub>SO<sub>4</sub>, finishing at 65 °C for 40 minutes), TLP-treated silk displayed a 16–20% improvement in crease recovery angle, with strong covalent bonding between TLP and

fibroin hydroxyl/amino groups. Spectroscopic analysis confirmed the crosslinking mechanism. The treatment preserved fabric strength (96% retention), maintained whiteness with minimal loss, and improved dye affinity while preserving softness. Importantly, anti-crease performance remained effective after multiple washes, underscoring TLP's eco-friendly potential for multifunctional silk finishing.

### Hydrophobic Properties of Fibrous Materials

Hydrophobic finishing of textiles is widely applied in household, technical, and protective fabrics. Durable hydrophobicity depends on reducing fiber surface energy and creating hierarchical roughness [72, 98, 104]. Surface energy reduction is often achieved with fluoropolymers, organosilicon derivatives, or ultrathin hydrophobic coatings applied through admicellar polymerization or direct fluorination [85, 96, 19]. Hydrophobicity is usually quantified by water contact angle (WCA), where values above 90° indicate hydrophobicity and >150° indicate super hydrophobicity [73]. However, due to fabric porosity, water absorption after immersion is a more reliable indicator [50, 56]. Effective hydrophobic coatings must balance repellency with breathability, softness, and wash durability [106, 78].

Polytetrafluoroethylene (PTFE) and fluoroalkylsilanes are among the most effective hydrophobizers [139, 113, 93]. Other methods include sol-gel coatings [30], nanoparticle-based finishes [87, 142] and ultrathin plasma or CVD coatings [143, 135]. Although nanoparticles can improve repellency, thick deposits may reduce fabric flexibility and comfort [109, 100]. Consequently, ultrathin coatings with hierarchical structures are favored. Recent trends also explore structural engineering of fabrics-modifying weave density, fiber diameter, and compactness-to-achieve hydrophobicity without chemical additives [91, 52].

### Antimicrobial Properties of Fibrous Materials

Antimicrobial finishing is essential for preventing microbial contamination that leads to fiber degradation, odour and health risks [33]. Treatments are categorized into biocidal (microbe-killing) and biostatic (growth-inhibiting) [124, 148]. Testing methods include qualitative streak assays (e.g., AATCC 147) and quantitative protocols such as AATCC TM100 and JIS L 1902, which are considered the most reliable [59, 102].

Antimicrobial agents can be incorporated during fiber production or applied during finishing. While internal incorporation limits options, finishing allows the use of metals, quaternary ammonium compounds, triclosan, antibiotics, and bio-based agents [107, 40]. However, concerns over toxicity and resistance have shifted focus to nanomaterials such as silver, zinc oxide, and titanium dioxide nanoparticles, which offer broad-spectrum antimicrobial activity and low resistance risk [43, 133].

Nanoparticle performance depends on size, shape, and dosage, with excessive loading impairing breathability and durability [131, 105]. To enhance fixation, sol-gel deposition, plasma pre-treatments, and ultrasonic-assisted *in situ* synthesis are used [13, 38, 94]. Encapsulation technologies using cyclodextrins, liposomes, and dendrimers-further improve wash resistance and controlled release [82, 9, 127].

Recent innovations include embedding silver nanoparticles in cross-linked polysiloxane coatings [33] and integrating iron oxide nanoparticles into polypropylene fibers within PTFE coatings, producing highly durable antimicrobial textiles [103].

These advances demonstrate a shift from conventional chemical finishes to nanotechnology- and encapsulation-based strategies that balance antimicrobial efficacy with fabric comfort, breathability and long-term durability.

### 5. Structural and Analytical Techniques in Silk Chemistry

Circular Dichroism (CD) spectroscopy is widely used to probe the secondary structures of silk proteins such as  $\alpha$ -helices and  $\beta$ -sheets, by monitoring UV light absorption [81]. Complementary to this, Fourier-transform infrared (FTIR) and Raman spectroscopy provide vibrational information from peptide backbones, identifying amide bands that correspond to silk's secondary structural motifs [34, 99]. These techniques can be applied to both silk gland contents and solid fibers, making them useful for monitoring structural transitions during spinning and post-processing [3].

### Nuclear Magnetic Resonance (NMR) Spectroscopy

Nuclear Magnetic Resonance (NMR) spectroscopy, in both solution and solid-state forms, is a powerful technique for resolving silk protein secondary and tertiary structures while also providing molecular dynamics insights. It is particularly effective for elucidating fibroin conformations in silk glands and in spun fibers, thereby linking structural organization with functional properties [7, 5].

### X-ray Scattering

X-ray scattering methods are extensively employed to investigate silk fiber structure at multiple hierarchical levels. Wide-angle scattering detects crystalline  $\beta$ -sheet nanocrystals, while small-angle scattering captures nanoscale ordering and amorphous features. Bragg diffraction peaks, crystallinity indices and orientation parameters derived from these analyses are essential for characterizing crystalline-amorphous balance in silk [20, 144, 17, 67, 31].

**Small-Angle X-ray Scattering (SAXS)** provides nanoscale details about the spacing and distribution of ordered and disordered regions, clarifying how nanostructural arrangements influence extensibility and strength [66, 36, 17].

**Wide-Angle X-ray Scattering (WAXS)** complements SAXS by focusing on the crystalline fraction, particularly  $\beta$ -sheet nanocrystals, which impart mechanical strength [12, 44, 145]. Together, SAXS and WAXS provide a holistic view of silk's hierarchical structural organization.

### Microscopy: SEM, AFM, and TEM

Scanning Electron Microscopy (SEM) enables visualization of silk fiber surface morphology at ~20 nm to 1  $\mu$ m resolution, highlighting features such as fibril orientation, bundling, surface striations, and damage [75, 8]. Atomic Force Microscopy (AFM) extends this analysis to nanometer resolution, enabling imaging of cross-sections and direct measurement of nanoscale mechanical properties. Transmission Electron Microscopy (TEM) offers even higher resolution for probing internal fiber structures, including differentiation between protein core and sheath [123, 18]. Collectively, these techniques are indispensable for unravelling silk's hierarchical architecture.

## Thermal Analysis: DSC and TGA

Thermal analysis provides insights into silk stability and phase transitions. Differential Scanning Calorimetry (DSC) measures transitions such as the glass transition (~423 K), crystallization, and melting of  $\beta$ -sheet structures [24, 54]. These transitions differ depending on silk type and environmental conditions, particularly humidity [84, 16]. Thermogravimetric Analysis (TGA) complements DSC by quantifying mass loss under controlled atmospheres, identifying decomposition profiles and intrinsic thermal stability [53, 84].

## Mechanical Testing

Tensile testing characterizes silk's viscoelastic behaviour, producing stress-strain curves that reveal strength, extensibility, stiffness and toughness. The initial elastic phase corresponds to amorphous matrix stretching, while strain stiffening is linked to  $\beta$ -sheet nanocrystal reorganization [25, 141]. Differences in extensibility and toughness across silkworm and spider silks are strongly correlated with their hierarchical molecular structures [108, 89].

## 6. Challenges and Opportunities

The textile chemistry of sericulture faces several challenges in maintaining fiber integrity and ensuring sustainability. Conventional soap-alkali degumming, while effective, can partially hydrolyze fibroin polypeptides, reducing tensile strength, crystallinity and thermal stability. Strong alkaline conditions also generate high effluent loads, posing environmental concerns. Achieving uniform dye fixation on silk remains another challenge due to the weak ionic and hydrogen bonding interactions, which may reduce wash and light fastness. Furthermore, large-scale industrial adoption of eco-friendly enzymatic and microbial degumming processes is limited by cost, enzyme stability and scalability. Balancing performance with sustainability in dyeing and finishing processes, especially when replacing synthetic dyes and toxic mordants with natural or bio-based alternatives, also presents technical and economic difficulties.

Despite these limitations, sericulture offers significant opportunities for innovation. Enzymatic and microbial degumming methods, as well as genetically engineered silkworms capable of self-degumming, provide eco-friendly solutions that preserve fibroin quality while reducing processing steps and environmental impact. Advances in nanotechnology open possibilities for antimicrobial, UV-protective and hydrophobic functional finishing of silk fabrics. Natural dyes, coupled with bio-mordants, present sustainable alternatives with cultural and ecological value. Additionally, the biomedical and cosmetic applications of sericin and fibroin—including wound healing, drug delivery, and tissue engineering—highlight the potential of silk beyond traditional textiles. Integration of spectroscopic and nanotechnological tools offers pathways to enhance fiber characterization and functionalization, bridging sericulture with high-value industrial and medical applications.

## 8. Future Scope

Future research should focus on the large-scale industrial optimization of enzymatic and microbial degumming technologies to replace conventional alkaline methods. Genetic engineering of silkworms for self-degumming and value-added

silk production holds strong potential for sustainable sericulture. The use of nanotechnology for multifunctional finishes such as antimicrobial, UV-protective, and hydrophobic properties will expand high-performance silk textiles. Greater exploration of bio-mordants and natural dyes can significantly reduce chemical pollution in textile processing. Additionally, expanding biomedical applications of silk fibroin and sericin in tissue engineering, wound healing, and drug delivery will strengthen silk's role as a next-generation biomaterial.

## 9. Conclusion

The textile chemistry of sericulture represents a unique intersection of tradition and innovation. While conventional processes raise concerns over fiber degradation and environmental sustainability, emerging enzymatic, microbial, and genetic approaches offer promising alternatives. Advances in eco-friendly dyeing, functional finishing, and nanotechnology are expanding the scope of silk textiles from luxury fabrics to multifunctional materials. Moreover, the biomedical and cosmetic potential of silk proteins underscores the versatility of sericulture in modern science and industry. Addressing current challenges through sustainable innovations will be critical in ensuring that silk maintains its cultural heritage while adapting to global demands for green and multifunctional materials.

**Conflict of Interest:** None Declared

## Ethical Approval

This article does not contain any studies with human participants or animals performed by any of the authors.

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