DURABLE ANTIBACTERIAL SILK FABRICS VIA DIP-COATING: DIALDEHYDE STARCH-MEDIATED IMMOBILIZATION OF CHITOSAN

Md Shariful Islam[1], Khurshid Alam[1], Mst Atia Rabbi[1], Md Sagor Islam[2], Md Mahmudul Hasan[2], Shaharia Ahmed'[1*]

[1] College of Textile and Clothing, Qingdao University, Qingdao-266101, China
[2] Research Institute of Textile and Clothing Industry, Zhongyuan University of Technology, Zhengzhou-451191, China
[*] Email: engr.shaharia@gmail.com, ORCID ID: https://orcid.org/0000-0003-1325-116X

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Abstract: *Developing durable and nontoxic antibacterial finishes for natural textiles remains a significant challenge. In this study, bio-derived dialdehyde starch (DAS) was used as a green crosslinker to introduce aldehyde groups onto silk fibers, enabling covalent immobilization of chitosan via Schiff-base reactions through a simple water-based dip-coating process. The grafting yield of aldehyde groups and chitosan was optimized with time and concentration, obtained after 3 h DAS treatment followed by immobilization with 2.0 wt% chitosan and 4 h batching. Aldehyde incorporation was verified by hydroxylamine titration, while chitosan grafting was confirmed by Raman spectroscopy, XPS, and SEM, and further quantified using a bicinchoninic acid (BCA) assay. The modified silk exhibited excellent antibacterial activity (>99.99% reduction against Escherichia coli and Staphylococcus aureus), while untreated silk showed no antibacterial effect. The fabrics retained over 96% antibacterial efficiency after 20 laundering cycles due to stable covalent bonding of chitosan. Meanwhile, hand feel, air permeability, and moisture permeability remained largely unchanged, indicating surface-confined modification. To sum up, this water-based carbohydrate-mediated finishing strategy provides an environmentally friendly route for durable antibacterial silk textiles.*

Keywords: Silk, Dialdehyde starch, Chitosan immobilization, Schiff-base reaction, Antibacterial textiles.

POSTOJANE ANTIBAKTERIJSKE SVILENE TKANINE IZRAĐENE METODOM POTAPANJA: IMOBILIZACIJA HITOZANA POSREDOVANA DIALDEHIDNIM SKROBOM

Apstrakt: *Razvoj postojanih i netoksičnih antibakterijskih završnih obrada za prirodne tekstile ostaje značajan izazov. U ovoj studiji, biološki dobijeni dialdehidni skrob (DAS) je korišćen kao zeleni umreživač za uvođenje aldehidnih grupa na svilena vlakna, omogućavajući kovalentnu imobilizaciju hitozana putem Šifovih bazanih reakcija jednostavnim postupkom premazivanja potapanjem na bazi vode. Prinos kalemljenja aldehidnih grupa i hitozana je optimizovan vremenom i koncentracijom, dobijen nakon 3 sata DAS tretmana, nakon čega je usledila imobilizacija sa 2,0 težinskih% hitozana i 4 sata doziranja. Ugradnja aldehida je verifikovana titracijom hidroksilamina, dok je kalemljenje hitozana potvrđeno Ramanovom spektroskopijom, XPS i SEM, a dalje kvantifikovano korišćenjem testa bicinhoninske kiseline (BCA). Modifikovana svila je pokazala odličnu antibakterijsku aktivnost*

(>99,99% smanjenje protiv Escherichia coli i Staphylococcus aureus), dok netretirana svila nije pokazala antibakterijski efekat. Tkanine su zadržale preko 96% antibakterijske efikasnosti nakon 20 ciklusa pranja zbog stabilnog kovalentnog vezivanja hitozana. U međuvremenu, osećaj na dodir, propustljivost vazduha i propustljivost vlage ostali su uglavnom nepromenjeni, što ukazuje na modifikaciju ograničenu na površinu. Ukratko, ova strategija završne obrade na bazi vode, posredovana ugljenim hidratima, pruža ekološki prihvatljiv put za izdržljive antibakterijske svilene tekstilne proizvode.

Ključne reči: svila, dijaldehidni skrob, imobilizacija hitozana, Šifova baza (Schiff-base reakcija), antibakterijski tekstil.

1. INTRODUCTION

Silk fibroin fibers are widely used in high-value textiles and biomedical materials due to their unique hierarchical structure, excellent mechanical performance, moisture-management capability, and inherent biocompatibility [1]. The molecular architecture of silk fibroin consists of repetitive glycine-alanine-rich sequences that self-assemble into highly ordered β-sheet crystallites dispersed within amorphous domains. This semicrystalline organization provides high tensile strength, flexibility, and durability [2]. However, the proteinaceous composition and hydrophilic surface chemistry of silk promote microbial adhesion and proliferation under humid conditions. Accumulation of microorganisms on textile substrates can cause odor generation, fiber degradation, and potential hygienic concerns, particularly in clothing and medical textile applications. Consequently, developing durable antibacterial silk materials while preserving the intrinsic physicochemical properties of the fibers remains an important challenge in textile functionalization.

Microbial contamination on silk fabrics has traditionally been controlled using antimicrobial finishes such as metallic nanoparticles, quaternary ammonium compounds, and synthetic biocides. These agents exhibit strong bactericidal activity through mechanisms including reactive oxygen species generation, membrane disruption, and metal ion release [3]. However, their practical application is limited by potential cytotoxicity, environmental concerns, and poor washing durability, as many antimicrobial agents are retained on fiber surfaces only through weak physical adsorption. From an interfacial chemistry perspective, the absence of stable covalent bonding between antimicrobial agents and silk fibers leads to gradual leaching during laundering or prolonged use [4]. Consequently, developing bio-based antimicrobial systems capable of forming stable interactions with textile substrates has become an important research focus. Chitosan has emerged as a promising natural antimicrobial polymer due to its intrinsic antibacterial activity and favorable physicochemical properties. It is obtained by partial deacetylation of chitin and consists mainly of β-(1→4)-linked D-glucosamine units containing primary amino groups [5]. In addition, chitosan exhibits excellent film-forming ability, biodegradability, and biocompatibility, making it attractive for sustainable textile finishing. Though direct deposition of chitosan on silk primarily relies on hydrogen bonding and electrostatic interactions with silk fibroin, resulting in poor washing durability and limited long-term antibacterial performance.

In recent years, oxidized polysaccharides have attracted increasing attention as bio-derived crosslinking platforms for immobilizing functional biomolecules on protein substrates. Oxidation of polysaccharides containing vicinal hydroxyl groups generates reactive aldehyde functionalities capable of forming covalent linkages with amino-containing polymers or proteins. In particular, periodate oxidation selectively cleaves the C2-C3 vicinal diol groups of glucose units, producing dialdehyde structures that readily react with primary amines to form imine bonds via Schiff-base reactions [6]. This reaction provides an efficient and environmentally benign route for constructing covalently crosslinked polysaccharide-protein networks [7]. Dialdehyde starch (DAS), produced by periodate oxidation of native starch, is a representative oxidized polysaccharide for such applications. Native starch consists of amylose and amylopectin chains composed of α-D-glucopyranose units. Oxidative cleavage of the C2-C3 bond introduces dialdehyde groups that significantly enhance polymer reactivity, enabling covalent bonding with amino groups in proteins or amino-containing polymers. In addition to high reactivity, DAS exhibits good water dispersibility, biodegradability, and low toxicity. Its flexible polysaccharide backbone further facilitates the formation of interfacial polymer networks that act as coupling layers between natural fibers and functional biomacromolecules [8].

Several recent studies have investigated oxidized polysaccharide-mediated immobilization strategies for grafting bioactive molecules onto protein substrates.

Dialdehyde derivatives such as dialdehyde cellulose [9], dialdehyde pullulan [10], and dialdehyde starch [11] have been employed as multifunctional crosslinkers to anchor peptides, enzymes, or antimicrobial polymers onto textile fibers through Schiff-base reactions between aldehyde groups and primary amines. These systems provide notable advantages, including mild aqueous processing, renewable raw materials, and improved functional durability resulting from covalent attachment. However, many reported approaches involve multistep modification procedures or require elevated curing temperatures, which may adversely affect the mechanical integrity, softness, and air permeability of silk fabrics [12]. Furthermore, achieving simultaneously high antibacterial efficiency and strong washing durability using entirely bio-derived components remains a significant challenge.

This study presents a carbohydrate-based interfacial immobilization strategy to fabricate durable antibacterial silk fabrics using dialdehyde starch (DAS) as a bio-derived crosslinker for chitosan fixation. Silk fabrics were first treated with DAS to introduce reactive aldehyde groups on the fiber surface, followed by covalent immobilization of chitosan through Schiff-base reactions between DAS aldehyde groups and the primary amino groups of chitosan. The resulting polysaccharide crosslinked network firmly anchors the antimicrobial polymer onto the silk substrate, enhancing immobilization stability and washing durability. Moreover, the water-based dip-coating process provides a simple and scalable finishing route compatible with industrial textile processing, offering a sustainable strategy for producing durable antibacterial silk fabrics based on renewable carbohydrate chemistry.

2. EXPERIMENTAL SECTIONS

2.1 Materials

Degummed silk fabric (plain weave 1 × 1, areal density 90 g m^{-2}) was supplied by Qingdao Meiya Textile Co., Ltd. (Qingdao, China). Dialdehyde starch (DAS) was obtained from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Chitosan was purchased from Macklin Biochemical Co., Ltd. (Shanghai, China). A bicinchoninic acid (BCA) protein assay kit was provided by Beyotime Biotechnology (Hangzhou, China). All other chemicals and reagents were of analytical grade and used as received without further purification.

2.2 Preparation of DAS silk fabric

DAS was dissolved in hot water with continuous stirring to obtain a homogeneous solution. Silk samples (10 × 10 cm) were immersed in the DAS solution (0.5–5.0 wt%), ensuring full wetting. The fabrics were kept at 25 °C for 1-6 hours to allow aldehyde groups to form on the surface, then rinsed thoroughly with deionized water to remove excess DAS. Afterward, the samples were dried at 60 °C for 1 hour and stored in sealed polyethylene bags at room temperature to promote further Schiff-base reactions between the aldehyde groups and amino groups in silk fibroin.

2.3 Quantification of aldehyde groups on silk

The aldehyde content on the silk was measured using hydroxylamine hydrochloride (HA·HCl) titration. Both treated and untreated samples were placed in 50 mL of 0.2 mol/L methanolic HA·HCl solution with eight drops of 0.1% bromothymol blue indicator. The mixtures were then titrated with 0.03 mol/L NaOH until a stable green color remained for 30 seconds. The aldehyde amount was calculated using the following formula

$$A\left(\frac{mmol}{g}\right) = \frac{30 \times (V2 - V1)}{m} \quad (1)$$

Where (A, mmol/g) is the aldehyde amount, V_2 and V_1 are the NaOH volumes for treated and control samples, respectively, and m is the fabric mass (g).

2.4 Preparation of DAS-chitosan silk fabric

Chitosan was applied using a dip-coating process. The DAS-treated silk was immersed in chitosan solutions (0.5-5.0 wt%) at 20 °C, and the liquid pickup was measured after padding to determine how much solution the fabric absorbed. The samples were then incubated at 25 °C for 1-10 hours to enable Schiff-base bonding between aldehyde groups. The primary amine groups (-NH_2) of chitosan react with the aldehyde groups of DAS-modified silk to form imine (Schiff-base, -C=N-) bonds, resulting in covalent immobilization. Excess chitosan was removed by ultrasonic washing in 0.5% SDS for 30 minutes, and rinsed with deionized water. Finally, the fabrics were dried at 60 °C for 1 hour.

2.5 Quantification of Grafted Chitosan Content

The grafted chitosan content on silk fabrics was quantified using the bicinchoninic acid (BCA) assay. Chitosan contains abundant primary amine groups (-NH_2) that can participate in redox reactions. Therefore, the BCA assay can be employed for quantitative analysis of amine-containing polymers such as chitosan. The amount of chitosan stable on the fabric was determined by measuring how much chitosan remained in the rinse solution by using the BCA pro-

tein assay. 0.15 mL portion of the SDS rinse solution was mixed with 3.0 mL of BCA reagent, vortexed, and heated at 37 °C for 30 minutes. The absorbance at 562 nm was calculated and the chitosan concentration was obtained from a calibration curve (0.02–0.50 mg/mL). The chitosan content per gram of fabric was then calculated using the following formula:

$$Qi\left(\frac{mg}{g}\right) = \alpha C0 - \frac{100C1}{m} \quad (2)$$

Where αi is the liquid pickup rate (%), C_0 and C_1 are the initial and residual chitosan concentrations (mg/mL), and m is the fabric mass (g).

2.6. Characterizations

Surface chemical composition of the modified silk fabrics was analyzed using X-ray photoelectron spectroscopy (XPS) with an AXIS-Ultra DLD multifunctional X-ray photoelectron spectrometer (Shimadzu Ltd., Japan) operated at a power of 450 W. Survey spectra were collected to determine elemental composition, while high-resolution spectra were used to analyze chemical states associated with dialdehyde starch deposition and chitosan immobilization.

Raman spectroscopy was performed using a Renishaw in Via confocal Raman microscope (Renishaw Plc., UK) equipped with a 785 nm excitation laser. Spectra were recorded in the range of 400-1800 cm^{-1} to identify characteristic vibrational bands of silk fibroin and polysaccharide structures and to detect functional groups generated during the aldehyde amine coupling reaction.

Surface morphology of untreated and modified silk fibers was observed using a field-emission scanning electron microscope (Ultra-55, Carl Zeiss, Germany). Prior to observation, the samples were sputter-coated with a thin gold layer to improve surface conductivity.

The aldehyde content introduced after starch oxidation was determined using the hydroxylamine hydrochloride titration method. The amount of chitosan immobilized on the silk fabrics was quantified using a bicinchoninic acid (BCA) assay based on the formation of a Cu^{+} bicinchoninic acid complex measured by UV-visible spectroscopy.

Antibacterial activity of the fabrics was evaluated by determining the bacterial reduction rate through comparison of viable bacterial counts before and after contact with the samples. The durability of antibacterial performance was further examined after repeated laundering cycles following standard textile washing procedures.

To evaluate the influence of the finishing treatment on comfort properties, air permeability, moisture vapor transmission, and fabric handle were measured. Air permeability was determined using a standard air permeability tester under controlled environmental conditions (20 ± 2 °C and 65 ± 4% relative humidity). Moisture vapor transmission was measured by the desiccant method according to GB/T 12704.1-2009. Fabric handle parameters, including softness, stiffness, smoothness, and drape, were evaluated using an FES-3 PhabrOmeter fabric hand evaluation system (PhabrOmeter, USA) in accordance with AATCC 202-2014. All measurements were conducted in triplicate and the average values were reported.

3. RESULTS & DISCUSSIONS

3.1 Fabrication and structural characterization of DAS-Chitosan-silk

The antibacterial modification of silk fabrics was achieved through a sequential dip-coating strategy using dialdehyde starch (DAS) as a reactive polysaccharide crosslinker for chitosan immobilization. Periodate oxidation of starch cleaves the C2-C3 vicinal diol bond of the glucopyranose units, generating dialdehyde groups along the polymer backbone. These aldehyde functionalities provide highly reactive sites capable of forming Schiff-base linkages with primary amino groups. During the modification process, DAS was first deposited onto the silk surface, introducing aldehyde groups that can react with the amino functionalities present in silk fibroin. Subsequent treatment with chitosan enabled further aldehyde amine reactions between the remaining aldehyde groups of DAS and the primary amino groups of chitosan, leading to the formation of covalent imine (-C=N-) bonds. As a result, a crosslinked DAS-chitosan polysaccharide network (see Fig. 1) was established on the silk fiber surface, providing a stable platform for durable functionalization.

The chemical evolution of the fiber surface during this modification process was investigated by X-ray photoelectron spectroscopy (XPS). The survey spectrum of pristine silk displayed the characteristics C1s, O1s, and N1s signals associated with the peptide structure of silk fibroin. The high-resolution N1s spectrum of untreated silk (see Fig. 2a-c) showed two dominant peaks located at 398.5 eV and 401.2 eV, corresponding to amide (-NH-) and amine ($-NH_2$) groups, respectively. These signals originate from the peptide backbone of fibroin and confirm the presence of nitrogen-containing functional groups on the silk surface. After DAS treatment, noticeable changes appeared in the N1s spectrum (refer to Fig. 2d), indicat-

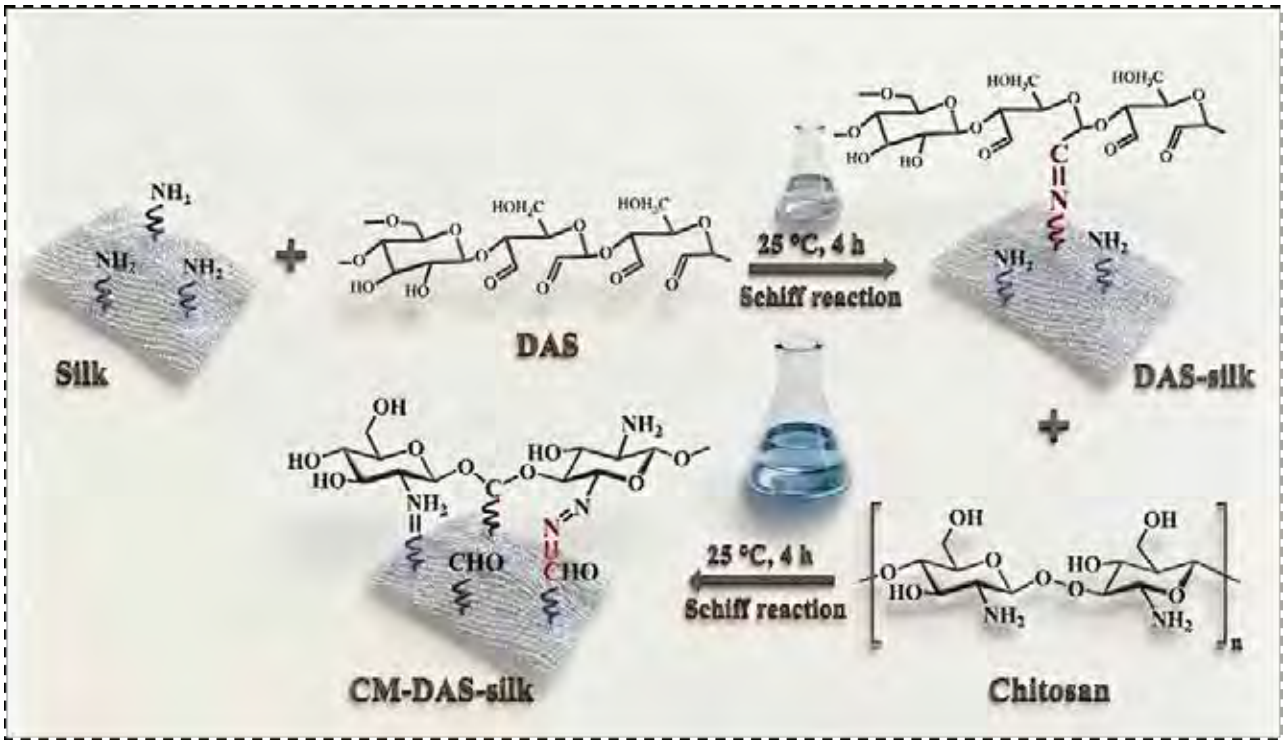

Figure 1: Schematic preparation of the CM-immobilized silk fabric via cross-linking with DAS.

ing chemical modification of the fiber surface. A new component corresponding to imine (-C=N-) bonding emerged, which is attributed to the Schiff-base reaction between the aldehyde groups of DAS and the amino groups present on the silk surface. Simultaneously, a relative decrease in the amide signal was observed, suggesting partial participation of surface amino functionalities in the crosslinking reaction. The O1s spectrum also exhibited an increase in oxygen intensity following DAS treatment, reflecting the introduction of oxygen-rich aldehyde groups derived from oxidized starch. These results collectively confirm the successful deposition of DAS and the formation of covalent linkages between the oxidized polysaccharide and silk fibroin.

Further modification was achieved through chitosan immobilization, which resulted in additional changes in the N1s spectrum (See Fig. 2e). The relative intensity of the $–NH_2$ component increased after chitosan treatment due to the presence of abundant primary amino groups in the chitosan structure. At the same time, a slight increase in the imine (-C=N-) signal was detected, indicating that remaining aldehyde groups of DAS further reacted with amino groups of chitosan through Schiff-base coupling. These spectral changes demonstrate the sequential formation of covalent linkages during DAS grafting and subsequent chitosan immobilization, leading to an increased density of nitrogen-containing functional groups on the silk surface.

Raman spectroscopy was employed to further verify the structural changes associated with the stepwise modification process. The Raman spectrum of pristine silk displayed characteristic fibroin bands related to the molecular structure and β-sheet conformation of silk. After DAS modification, a new peak appeared at 1728 cm^{-1}, which corresponds to the C=O stretching vibration of aldehyde groups introduced by dialdehyde starch. The presence of this band confirms the successful oxidation of starch and its subsequent attachment to the silk surface. Following chitosan immobilization, additional spectral features were observed in the Raman spectrum of the DAS-silk-chitosan sample as illustrated in Fig. 3. Two new bands appeared at 1584 cm^{-1} and 1390 cm^{-1}. The band near 1584 cm^{-1} is attributed to the stretching vibration of imine (C=N) bonds formed during Schiff-base reactions, whereas the band around 1390 cm^{-1} corresponds to C-N stretching vibrations associated with the chitosan structure [13]. The increased intensity of the C-N band indicates successful incorporation of the amino-rich chitosan polymer onto the silk surface. Moreover, a partial decrease in the aldehyde-related band intensity after chitosan treatment suggests consumption of aldehyde groups during imine bond formation. The combined XPS and Raman analyses clearly demonstrate the successful stepwise construction of the DAS-chitosan coating on silk fibers. Dialdehyde starch first introduces reactive aldehyde functionalities onto the silk surface, which subsequently react

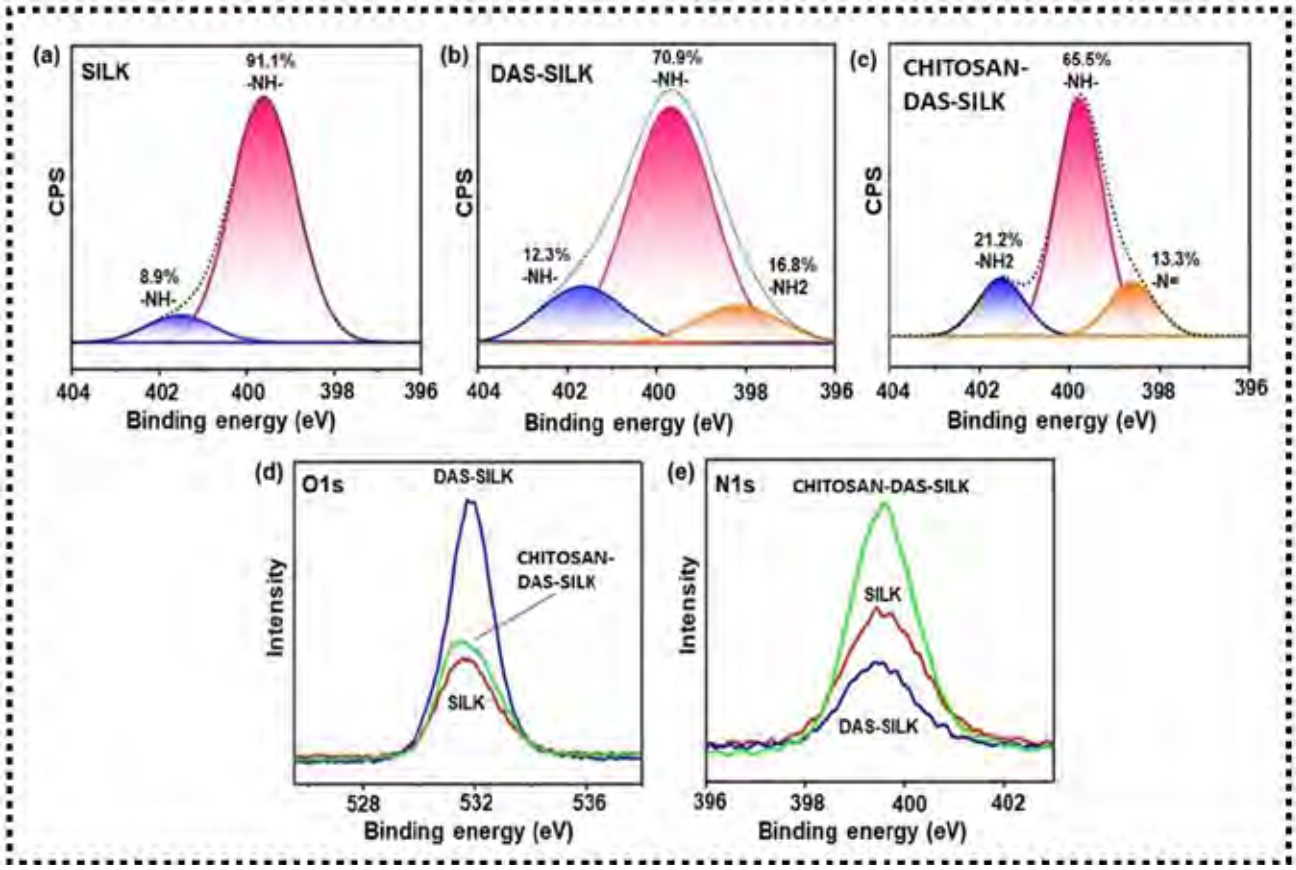

Figure 2: XPS spectra of (a) pristine silk, (b) DAS-modified silk, and (c) DAS-chitosan-treated silk; (d) O1s spectra and (e) N1s spectra.

with the amino groups of chitosan to form stable imine linkages. The resulting DAS-chitosan interfacial network forms a covalently anchored polysaccharide layer on the silk surface, providing a structural foundation for enhanced antibacterial functionality and improved durability of the treated fabrics.

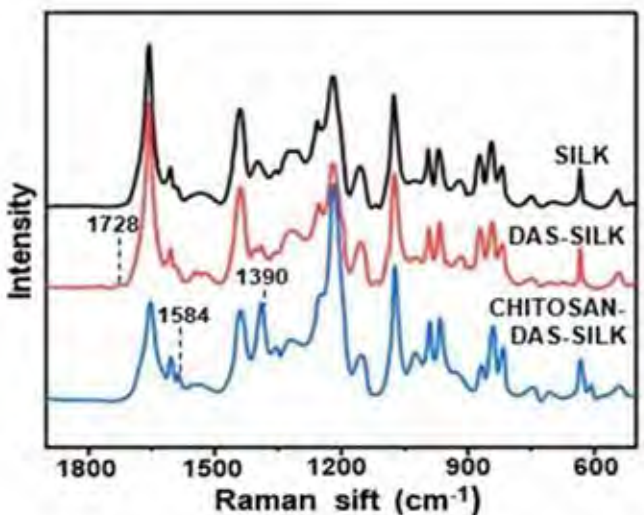

Figure 3: Raman spectra of pristine silk, DAS-modified silk, and DAS-chitosan-treated silk

3.2 Grafting process optimization

The efficiency of the DAS-chitosan modification was strongly influenced by the formation of aldehyde groups on the silk surface and the subsequent immobilization conditions of chitosan. Therefore, the effects of reaction time during dialdehyde starch treatment, as well as chitosan concentration and batching time, were systematically investigated to determine the optimal grafting conditions. The aldehyde content introduced onto the silk fabrics after DAS treatment was quantified using the hydroxylamine hydrochloride titration method. As shown in Fig. 4a-b, the aldehyde concentration increased progressively with reaction time, indicating continuous oxidation of starch and deposition of reactive aldehyde groups on the silk surface. The aldehyde content reached a maximum value of 35.56 ± 4.7 μmol g^{-1} after 3 h of reaction. Further extension of the reaction time resulted in no significant increase in aldehyde content, suggesting that the oxidation reaction approached equilibrium and the available reactive sites were largely consumed. Therefore, a reaction time of 3 h was selected as the optimal condition for generating sufficient aldehyde functionalities for subsequent chitosan immobilization.

The immobilization efficiency of chitosan was further evaluated by examining the influence of chitosan concentration and batching time. As illustrated in Fig. 4c-d, the amount of grafted chitosan increased gradually as the chitosan concentration increased from 0.5 wt% to 5.0 wt%, indicating that higher polymer concentrations promoted the interaction between chitosan amino groups and the aldehyde functionalities on the DAS-modified silk surface. Similarly, increasing the batching time from 1 h to 10 h enhanced the grafting amount, suggesting that longer reaction times allowed more extensive aldehyde–amine coupling through Schiff-base reactions.

However, the grafting amount showed a clear plateau beyond a certain condition. The optimal grafting efficiency was obtained at 2.0 wt% chitosan concentration with a batching time of 4 h, resulting in a chitosan loading of 12.3 mg g^{-1} on the silk fabric. Increasing the concentration or batching time beyond these values produced only marginal improvements in grafting amount. This behavior indicates that the available aldehyde groups introduced by DAS gradually became saturated with chitosan chains, limiting further immobilization. These results demonstrate that the grafting process is governed by the availability of reactive aldehyde groups and the accessibility of amino groups from chitosan. Under optimized conditions, sufficient aldehyde functionalities were generated on the silk surface and effectively utilized for covalent immobilization of chitosan, enabling the formation of a stable polysaccharide coating that is expected to contribute to enhanced antibacterial performance and durability.

3.3 Morphology analysis

The surface morphology of pristine silk, DAS-modified silk, and DAS-chitosan-treated silk fabrics was examined using scanning electron microscopy (SEM), and the results are shown in Fig. 5. The untreated silk fibers (see Fig. 5a) exhibited smooth and clean surfaces with well-defined filament structures, which is typical for degummed silk fibroin [14]. The absence of surface impurities indicates that the degumming process effectively removed sericin, leaving the fibroin fibers exposed. After modification with dialdehyde starch (see Fig. 5b), noticeable changes in the fiber surface morphology were observed. The silk fibers displayed a thin and slightly uneven coating layer accompanied by small particulate deposits. This morphological change is attributed to the adsorption and partial crosslinking of oxidized polysaccharide chains on the silk surface. The presence of this layer suggests

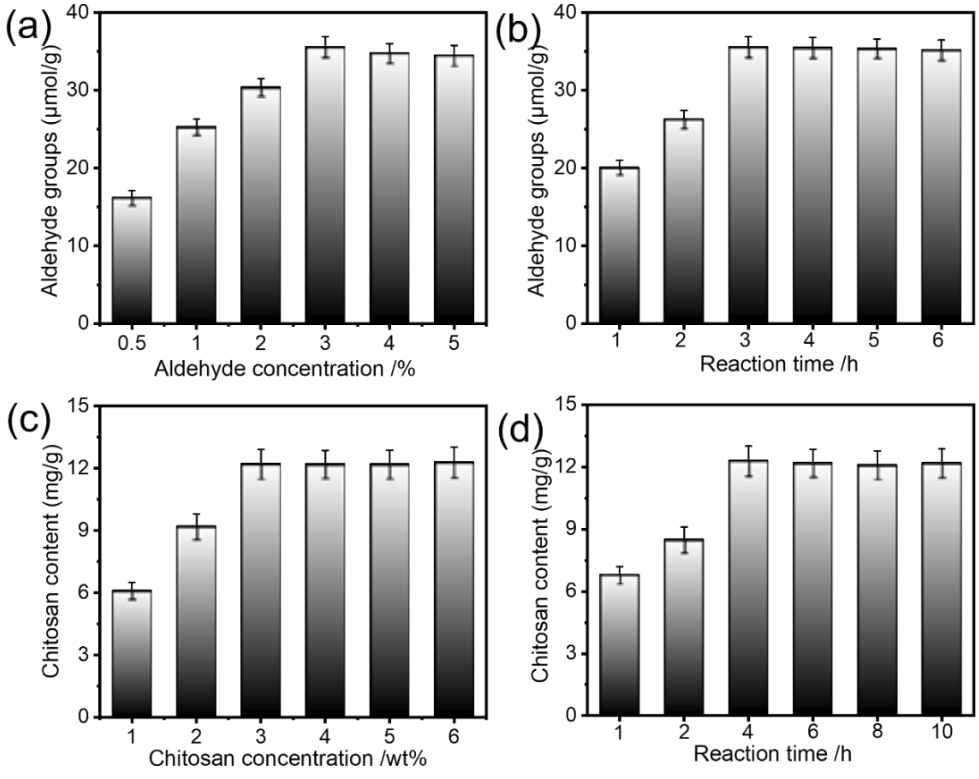

Figure 4: Optimization of grafting conditions, (a) aldehyde content, (b) effect of reaction time during DAS treatment, (c) effect of chitosan concentration on grafting amount, and (d) influence of batching time on chitosan immobilization on silk fabrics.

successful deposition of dialdehyde starch, which introduces reactive aldehyde groups capable of further chemical interaction.

Following chitosan immobilization (see Fig. 5c), the surface morphology changed significantly. The silk fibers were covered by a thicker and more continuous coating layer compared with the DAS-treated sample. The surface appeared more uniform, indicating that chitosan was effectively immobilized onto the aldehyde-functionalized silk through Schiff-base coupling reactions. The presence of the DAS layer likely facilitates the uniform distribution of chitosan by providing abundant reactive sites for covalent bonding. Despite the formation of the polysaccharide coating, the overall fibrous structure of silk remained intact, suggesting that the dip-coating modification did not cause structural damage to the fibers. These morphological observations are consistent with the spectroscopic results obtained from XPS and Raman analyses, further confirming the successful formation of a DAS-chitosan polysaccharide network on the silk fiber surface.

3.4 Antibacterial performance of chitosan-dialdehyde-silk

The antibacterial properties of the modified silk fabrics were evaluated against *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*), as shown in Fig. 6a-d. The untreated silk exhibited no measurable antibacterial activity, whereas the chitosan-DAS-silk fabrics produced clear inhibition zones against both bacteria, demonstrating effective antibacterial functionality after modification [15]. Among the prepared samples, the fabric treated with the optimal chitosan concentration showed the highest antibacterial performance, achieving more than 99.99% bacterial reduction. The antibacterial efficiency was strongly influenced by the chitosan concentration and reaction time during the modification process (Fig. 7a, b). As the chitosan concentration increased, the antibacterial reduction ratio improved significantly and reached a maximum at 2.0 wt%, which corresponds well with the highest grafting level of chitosan on the silk surface. Similarly, increasing the reaction time from 1 to 4 h gradually enhanced the antibacterial activity. This improvement is attributed to the progressive formation of Schiff-base bonds between the aldehyde groups of DAS and the primary amino groups of chitosan, which strengthens the covalent attachment of chitosan to the silk substrate. After 4 h of reaction, the antibacterial effect reached a plateau, suggesting that most of the available reactive sites had already participated in the bonding process.

The durability of the antibacterial treatment was further evaluated through repeated washing cycles (see Fig. 7c). The modified fabrics maintained more than 96% antibacterial efficiency even after 20 laundering cycles, indicating excellent washing stability. Only a slight decrease in activity was observed, which can be attributed to the removal of loosely adsorbed chitosan from the fiber surface, while the covalently bonded chitosan remained firmly attached to the silk fibers. In addition to antibacterial performance, the hydrophilicity of the modified fabric was examined through capillary wicking tests (See Fig. 6e). The chitosan-DAS-silk fabric retained strong hydrophilicity due to the presence of polar amino groups in chitosan. The capillary rise height increased from 15.5 cm for untreated silk to 17.3 cm for the modified fabric, indicating improved moisture transport capability. Dye uptake experiments also showed clearer and faster liquid migration, confirming the enhanced moisture wicking behavior of the treated silk. These results demonstrate that the incorporation of chitosan through the DAS-mediated covalent linkage effectively imparts strong antibacterial activity to silk fabrics while maintaining excellent hydrophilicity and washing durability. The antibacterial efficiency is primarily governed by chitosan concentration and reaction time, and the stable DAS–chitosan bonding ensures long-term functional performance of the modified silk textiles.

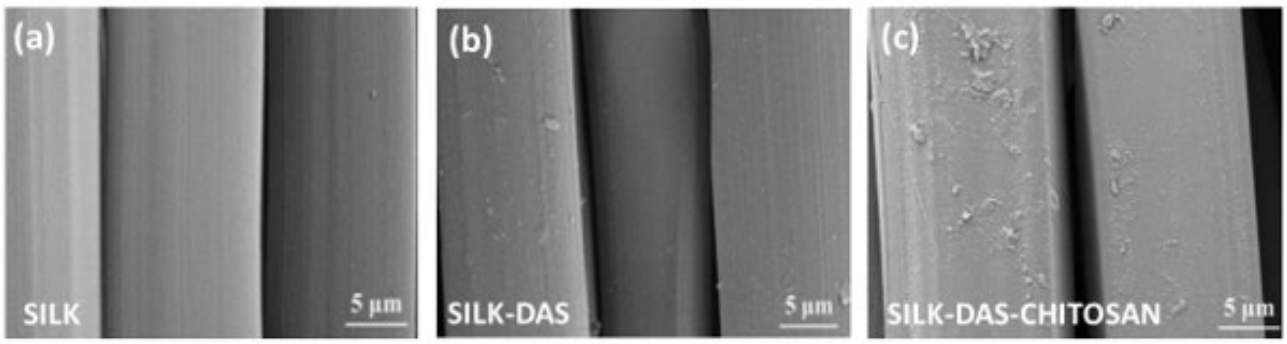

Figure 5: SEM images of (a) pristine silk, (b) DAS-modified silk, and (c) DAS–chitosan-treated silk fabrics.

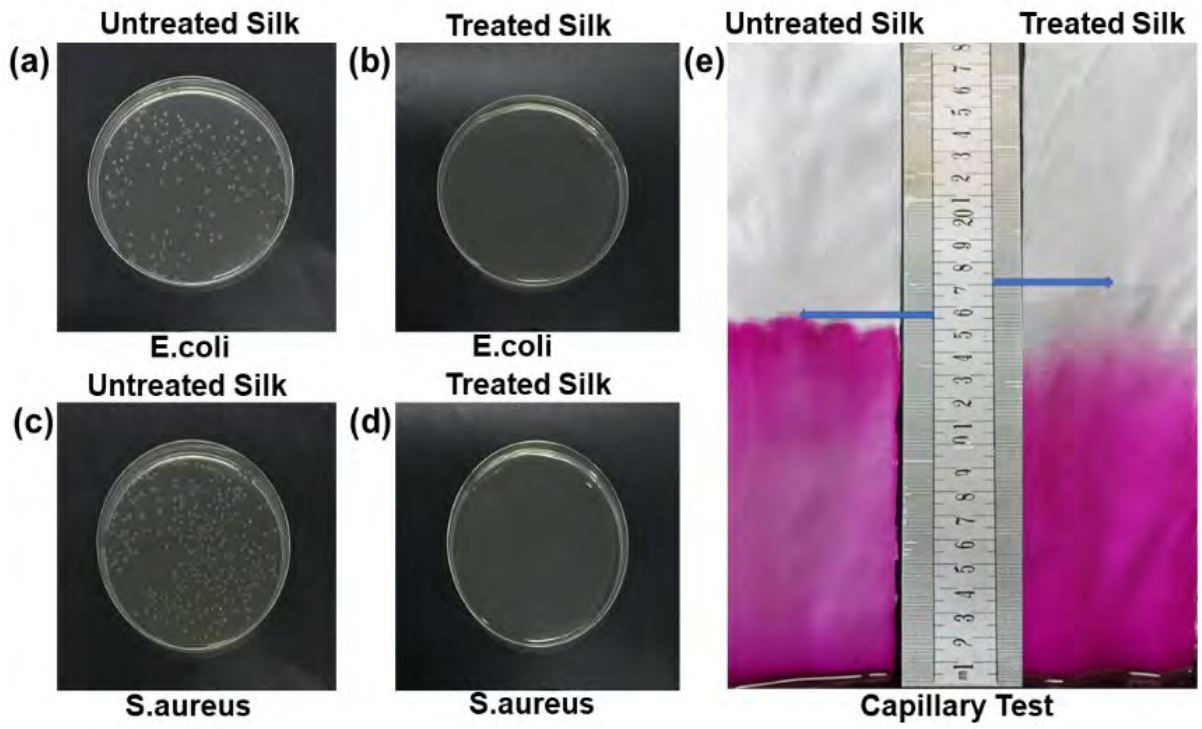

Figure 6: (a, c) Antibacterial test of unmodified silk against *E. coli* and *S. aureus*; (b, d) Antibacterial test of modified silk against *E. coli* and *S. aureus*; (e) Wicking test of modified and unmodified silk samples.

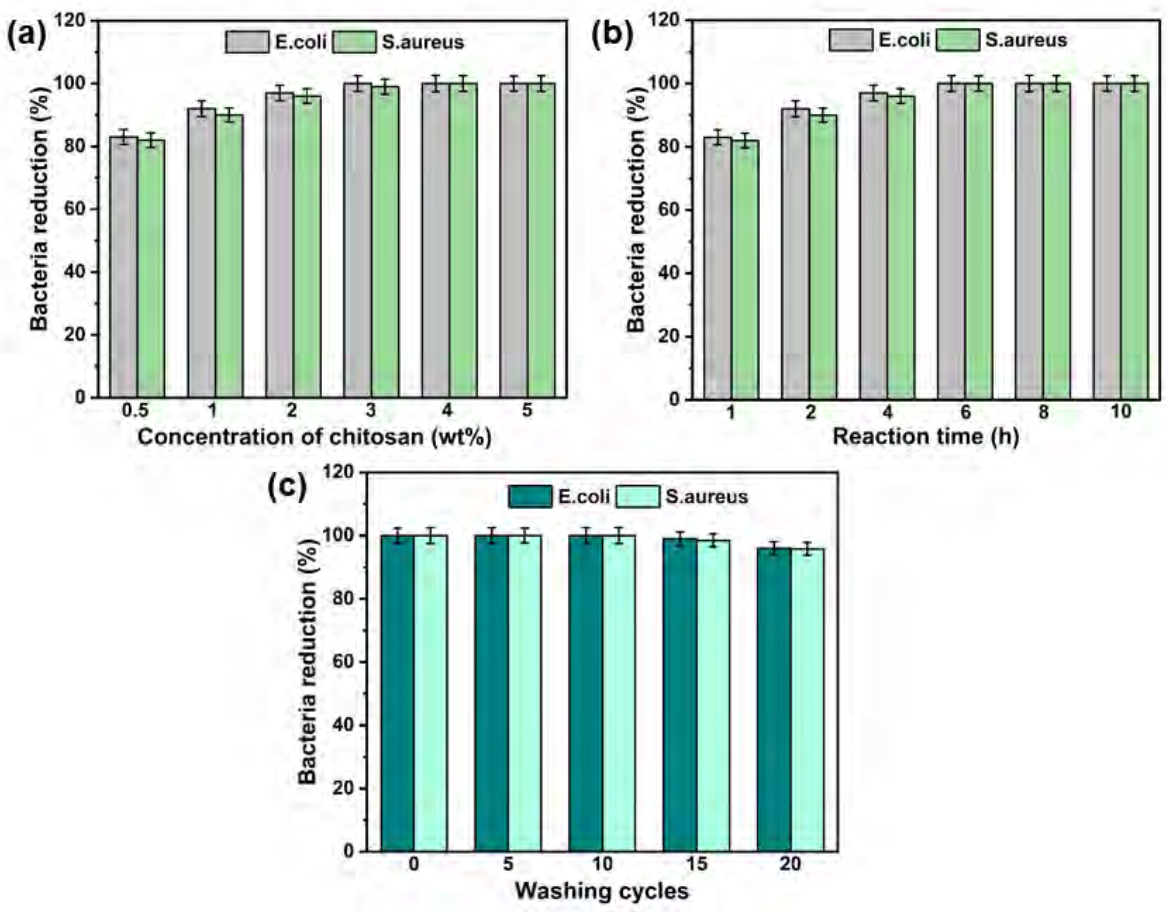

Figure 7: (a) Antibacterial reduction rates at different chitosan concentrations; (b) Effect of reaction time; (c) Effect of washing cycles on antibacterial performance.

3.5 Physical properties analysis

The influence of DAS-chitosan finishing on the fundamental physical properties of silk fabrics was systematically evaluated, and the results are summarized in Fig. 8. The modification process introduced only negligible changes to the intrinsic performance of silk, indicating that the antibacterial treatment primarily occurs at the fiber surface while preserving the bulk structure of the fibroin matrix. As shown in Fig. 8a, the tensile strength of the treated silk exhibits only a slight reduction compared with that of the untreated sample. This minor decrease suggests that the aldehyde-mediated crosslinking of DAS and the subsequent grafting of chitosan mainly occur on the outer surface of the silk fibers. Consequently, the internal molecular arrangement of silk fibroin remains largely unaffected, allowing the fabric to retain most of its original mechanical integrity.

The air permeability results (see Fig. 8b) further demonstrate that the DAS-chitosan modification does not significantly alter the porous structure of the silk fabric. The measured values remain nearly identical to those of untreated silk, indicating that the thin functional coating formed on the fiber surface does not obstruct inter-fiber pores or restrict air flow. Maintaining adequate air permeability is particularly important for ensuring breathability in textile applications. In addition, moisture permeability measurements (refer to Fig. 8c) reveal that the treated fabrics preserve a moisture transmission capacity comparable to that of the pristine silk. This observation suggests that the DAS-chitosan layer does not hinder the transport of water vapor through the fabric structure. The retention of moisture management capability is consistent with the hydrophilic nature of chitosan, which contains abundant polar amino groups that can facilitate moisture interaction.

The tactile properties of the fabrics were also evaluated through hand-feel analysis (see Fig. 8d). Parameters such as softness, stiffness, and smoothness show only minimal variation after treatment, indicating that the DAS-chitosan finishing does not significantly alter the characteristic softness and drape of silk. This result further confirms that the modification layer is thin and uniformly distributed, avoiding the formation of rigid coatings that could compromise fabric comfort. Collectively, these findings demonstrate that the DAS-chitosan finishing strategy successfully imparts antibacterial functionality while maintaining the essential physical attributes of silk fabrics. The treated silk retains its mechanical strength, breathability, moisture permeability, and natural hand feel, highlighting the suitability of this modification approach for advanced functional textile applications where both hygienic performance and wearer comfort are critical.

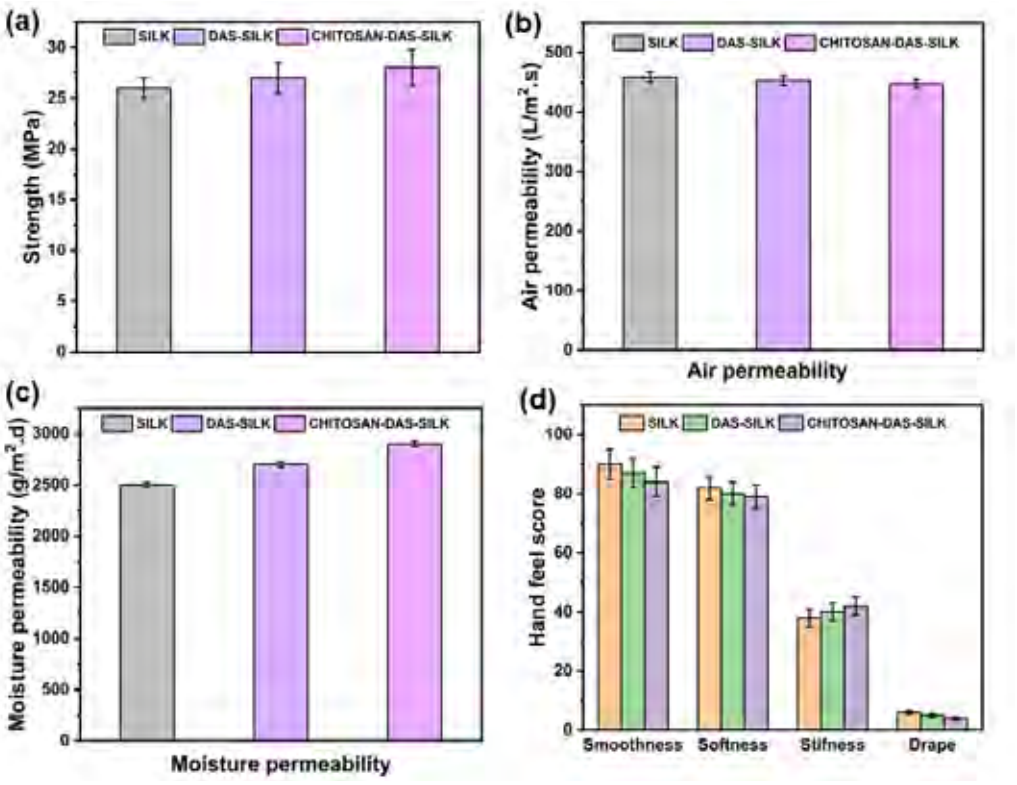

Figure 8: Physical properties of silk fabrics before and after DAS-chitosan treatment: (a) tensile strength, (b) air permeability, (c) moisture permeability, and (d) hand-feel properties.

4. CONCLUSION

In this work, a sustainable carbohydrate-based finishing strategy was developed to fabricate durable antibacterial silk fabrics through dialdehyde starch (DAS)-mediated covalent immobilization of chitosan. The sequential dip-coating process enabled the introduction of reactive aldehyde groups onto silk via DAS treatment, followed by the covalent grafting of chitosan through Schiff-base reactions. The successful formation of imine linkages and the uniform deposition of chitosan on the silk surface were confirmed by X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and scanning electron microscopy (SEM), demonstrating the effectiveness of the DAS crosslinking system in anchoring chitosan onto the fiber interface.

The modified fabrics exhibited excellent antibacterial performance, achieving bacterial reduction rates above 99.99% against *E. coli* and *S. aureus*, while untreated silk showed no antibacterial activity. The antibacterial efficiency was strongly dependent on chitosan concentration and reaction time, with optimal performance obtained at 2.0 wt% chitosan and 4 h batching, consistent with the observed grafting behavior. Importantly, the treated fabrics maintained more than 96% antibacterial efficiency after 20 laundering cycles, confirming the high durability of the covalently immobilized chitosan layer.

In addition to antimicrobial functionality, the DAS-chitosan modification preserved the essential comfort and physical properties of silk. The treated fabrics maintained comparable tensile strength, air permeability, moisture permeability, and hand feel relative to untreated silk. Capillary wicking and dye uptake experiments further indicated improved moisture transport due to the hydrophilic nature of chitosan. Overall, this study demonstrates that DAS-chitosan finishing provides an effective, metal-free, and water-based approach for producing durable antibacterial silk fabrics without compromising textile performance. The combination of strong antibacterial activity, excellent washing durability, and preserved comfort properties highlights the potential of this carbohydrate-mediated strategy for the development of sustainable hygienic textiles for apparel and biomedical applications.

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Credit Author Statement

Md Shariful Islam: Conceptualization, Methodology, Investigation, Writing-original draft, Khurshid Alam: Formal analysis, Resources, Writing-review & editing, Mst Atia Rabbi: Formal analysis, Data curation, Md Sagor Islam: Validation, Software**,** Md Mahmudul Hasan: Data curation, Validation, Shaharia Ahmed: Conceptualization, Visualization, Writing-original draft reviewing & editing, Supervision.

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