

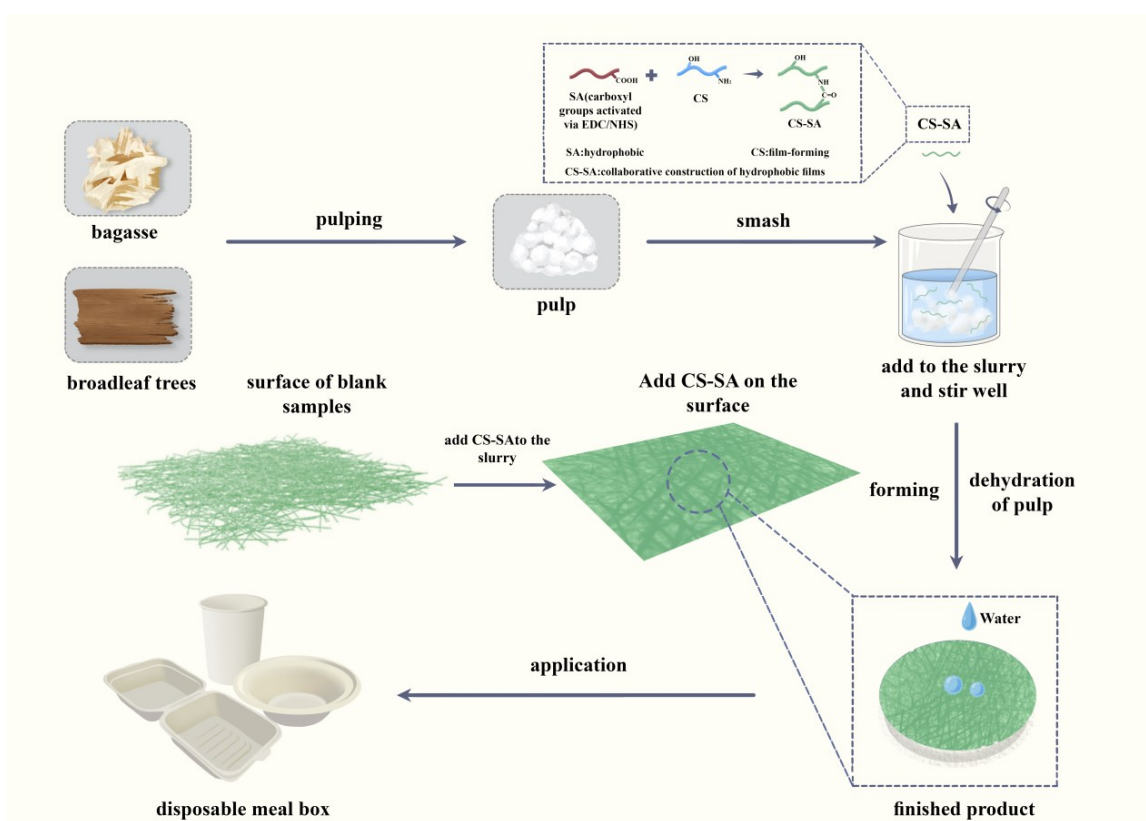
Preparation and Performance of a Green, Fluorine-Free Chitosan-Stearic Acid Waterproof Agent for Molded Pulp

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GRAPHICAL ABSTRACT



Preparation and Performance of a Green, Fluorine-Free Chitosan-Stearic Acid Waterproof Agent for Molded Pulp

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To develop a green, efficient, fluorine-free waterproof pulp molding material, this study incorporated chitosan-stearic acid graft copolymer (CS-SA) into the pulp fiber system *via* the conventional internal pulp addition method used in the papermaking industry. Compared with post-treatment surface techniques such as spraying and coating, adding the waterproofing agent directly into the pulp ensures its uniform distribution throughout the three-dimensional fiber network—from the pulp to the final product—while balancing the operational feasibility of paper manufacturing with the integrated waterproofing performance of the finished product. The research results demonstrated that CS-SA significantly enhanced the waterproof performance of the product (water contact angle 131°, Cobb value 12.9 g/m², no leakage or permeation at 100 °C water for 30 minutes). Systematic characterization revealed that CS-SA forms a dense hydrophobic film on the fiber surface and between fibers, which is the key to its high-efficiency waterproofing. In addition, the modified material exhibits low cytotoxicity and excellent antibacterial properties, ensuring safety for applications in food packaging. Its superior thermal stability guarantees effectiveness during processing steps such as pulp molding and hot pressing.

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Keywords: Chitosan-stearic acid grafted copolymer; Molded pulp; Hydrophobic agent; Wet-end addition

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INTRODUCTION

Spurred by the global implementation of plastic bans and growing consumer environmental awareness, molded pulp is gaining significant traction as a sustainable packaging material (Didone *et al.* 2017; Debnath *et al.* 2022; Istiqomah *et al.* 2024; Mondal *et al.* 2025). Typically fabricated from renewable plant fibers—such as wood pulp, bagasse, and bamboo pulp (Mamaye *et al.* 2019; Liu *et al.* 2020; Klayya *et al.* 2023; Zhu *et al.* 2024; Sun *et al.* 2025; Zaini *et al.* 2025), it offers the distinct advantages of biodegradability and recyclability (Curling *et al.* 2017; Didone and Tosello 2019; Lou and Gong 2022; Singh *et al.* 2023; Neng *et al.* 2025). These properties make it an ideal candidate for replacing plastic products (Xia *et al.* 2021; Qiu *et al.* 2025) in applications such as food packaging, electronics cushioning, and agricultural seedling containers (Semple *et al.* 2022; Zhang and Youngblood 2023; Gomez-Gijon *et al.* 2025). However, the inherent hydrophilicity and porous structure of plant fibers (Vrabič Brodnjak and Tihole 2020) make the final products susceptible to water absorption and penetration, leading to structural deformation and functional failure (Li *et al.* 2025b). This critical drawback severely impedes their application in moisture-sensitive areas, such as cold-chain food packaging and take-out

containers. Consequently, developing effective hydrophobic modification strategies is paramount to overcoming this performance bottleneck and expanding the market reach of molded pulp products.

Papermaking chemical additives serve as a crucial tool for regulating paper properties, optimizing production processes, and endowing paper with special functionalities. Their research and application have a long history. In recent years, the development of multifunctional and environmentally friendly additives has become a mainstream trend. However, existing additives still face challenges in practical applications, such as unclear mechanisms of interaction with fibers/fillers and cumulative ecological impacts associated with certain synthetic additives. Conventional waterproofing technologies for molded pulp primarily rely on fluorine-containing compounds, such as per- and polyfluoroalkyl substances (PFAS). These chemicals form a barrier with extremely low surface energy on fiber surfaces, thereby imparting excellent water and oil resistance to the material (Lendewig *et al.* 2025; Taliantzis and Ellinas 2025). Nevertheless, PFAS are recognized as persistent organic pollutants (Ofiera *et al.* 2025). They are known for their bioaccumulation potential in the environment and living organisms (Riedel *et al.* 2019; Hutcheson *et al.* 2020; Murillo-Gelvez *et al.* 2025; Sahu *et al.* 2025) and associated toxicity (Wang *et al.* 2019; Whitehead *et al.* 2021; Fang *et al.* 2025). Consequently, they are now subject to stringent global regulations, including relevant environmental policies in China, the EU's REACH regulation, and bans in multiple U.S. states, which explicitly restrict or prohibit their use in food-contact materials. This regulatory landscape has created a pressing demand within the industry to develop efficient, safe, and fluorine-free waterproofing alternatives for molded pulp.

Current non-fluorine additives primarily include polysaccharides, paraffin emulsions, acrylates, and protein-based waterproofing agents. The prevailing paradigm for waterproofing molded pulp depends on post-treatments like spraying or coating. Despite their operational simplicity, these techniques localize additives on the surface, frequently necessitating binders for coating adhesion. This approach inherently compromises the material's cost-effectiveness, manufacturing efficiency, and key properties such as breathability and biodegradability. Therefore, an in-process modification route that achieves integral waterproofing *via* robust bonding with fibers is highly desirable. The wet-end addition technique emerges as a compelling solution, whereby additives are incorporated directly into the pulp slurry. This ensures their homogeneous dispersion throughout the three-dimensional fiber network, effecting bulk modification. This one-pot strategy enhances process efficiency and economic viability by obviating additional post-treatment units. More importantly, the water-based processing environment affords ideal conditions for molecular-level interactions between the hydrophilic fibers and functional additives, potentially leading to a more durable and stable composite interface than what is achievable through superficial treatments.

Chitosan (CS), a renewable polysaccharide (Deng *et al.* 2022; Kjellgren *et al.* 2006) obtained from chitin deacetylation (Afrifa and Awuah 2026; Fang *et al.* 2017), is characterized by molecular chains rich in amino and hydroxyl groups. This unique structure underpins its multifunctionality: its cationic character confers antibacterial properties by disrupting microbial membranes (Jung *et al.* 2018; Dong *et al.* 2020; Gagon *et al.* 2020); it boasts proven biocompatibility and biodegradability (You *et al.* 2025; Chen *et al.* 2016; Munagapati *et al.* 2026; Li *et al.* 2025a); and it readily forms adherent films on fibers *via* electrostatics and hydrogen bonding (Grande *et al.* 2017; Shiekh *et al.* 2022), establishing it as a promising wet-end additive. Stearic acid (SA), a natural fatty acid, provides an

effective means to lower surface energy *via* its long alkyl chain (Yang *et al.* 2024). However, simply blending CS and SA through physical mixing results in poor compatibility due to their differing hydrophilic/hydrophobic properties. SA tends to migrate and precipitate, not only compromising waterproof stability but also potentially weakening the inter-fiber bonding strength. To circumvent this, chemical grafting creates a coherent CS-SA amphiphile. In this designed structure, the CS moiety serves as an anchor to the hydrophilic fiber substrate, while the grafted SA chains assemble into a dense, molecularly organized hydrophobic barrier, ensuring stable and intrinsic waterproofing.

While the intrinsic properties of chitosan (CS) and stearic acid (SA) are well-understood, the strategic use of a CS-SA graft copolymer as a wet-end additive for integral, fluorine-free waterproofing of molded pulp has been scarcely investigated. The current scientific landscape is dominated by surface-application methods. Examples include composite films with CS emulsions (Dai *et al.* 2025), single-layer coatings from Pickering emulsions (Peng *et al.* 2024), bilayer systems involving sprayed CS and soaked SA (Shen *et al.* 2024), CS-based composite coatings (Kansal *et al.* 2020; Shen *et al.*), and sophisticated multilayer architectures (Du *et al.* 2021). This prevailing focus on surface engineering stands in stark contrast to the unexplored potential of bulk modification through wet-end chemistry, which is the central focus of this work.

Therefore, this study aims to develop a high-performance, fully bio-based, and fluorine-free waterproofing strategy for molded pulp *via* the wet-end addition of a CS-SA graft copolymer. The authors systematically synthesized and characterized CS-SA using FTIR, XPS, and TGA. The influence of the SA grafting ratio on waterproofing efficiency was rigorously investigated by measuring Cobb values and WCA. The formation mechanism of the hydrophobic barrier was elucidated through SEM analysis. Furthermore, the material's suitability for food packaging was verified by assessing its antibacterial properties and cytotoxicity. This work provides fundamental insights and a practical green processing route to advance the sustainable development of the molded pulp industry.

EXPERIMENTAL

Materials

Stearic acid (SA) and absolute ethanol were procured from Sinopharm Chemical Reagent Co., Ltd. (China). Chitosan (CS, degree of deacetylation $\geq 95\%$, viscosity 100 to 200 mPa·s), N-Hydroxysuccinimide (NHS), and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC) were sourced from Sigma-Aldrich (USA). A second chitosan sample (CS₈₅, degree of deacetylation 85-90%, viscosity 105 mPa·s) was obtained from Qingdao Hehai Biological Technology Co., Ltd. (China). Thiazolyl blue tetrazolium bromide (MTT), phosphate-buffered saline (PBS), and agar powder were purchased from Beijing Solarbio Science & Technology Co., Ltd. (China). Tryptone and yeast extract were acquired from Thermo Fisher Scientific (China). Sodium chloride was supplied by Sichuan Xilong Scientific Co., Ltd. (China). Dimethyl sulfoxide (DMSO) was provided by Chongqing Chuandong Chemical (Group) Co., Ltd. (China). Glacial acetic acid (reagent grade, 99.5%) was obtained from Shandong Keryn Biochemical Co., Ltd. (China). All chemicals were used as received without further purification. The bleached pulp was purchased from Guangxi Qiaowang Paper Mold Products Co., Ltd.

Preparation of CS-SA Graft Copolymer

The CS-SA graft copolymers were synthesized following a literature procedure (Shamsheera *et al.* 2019) with modifications.

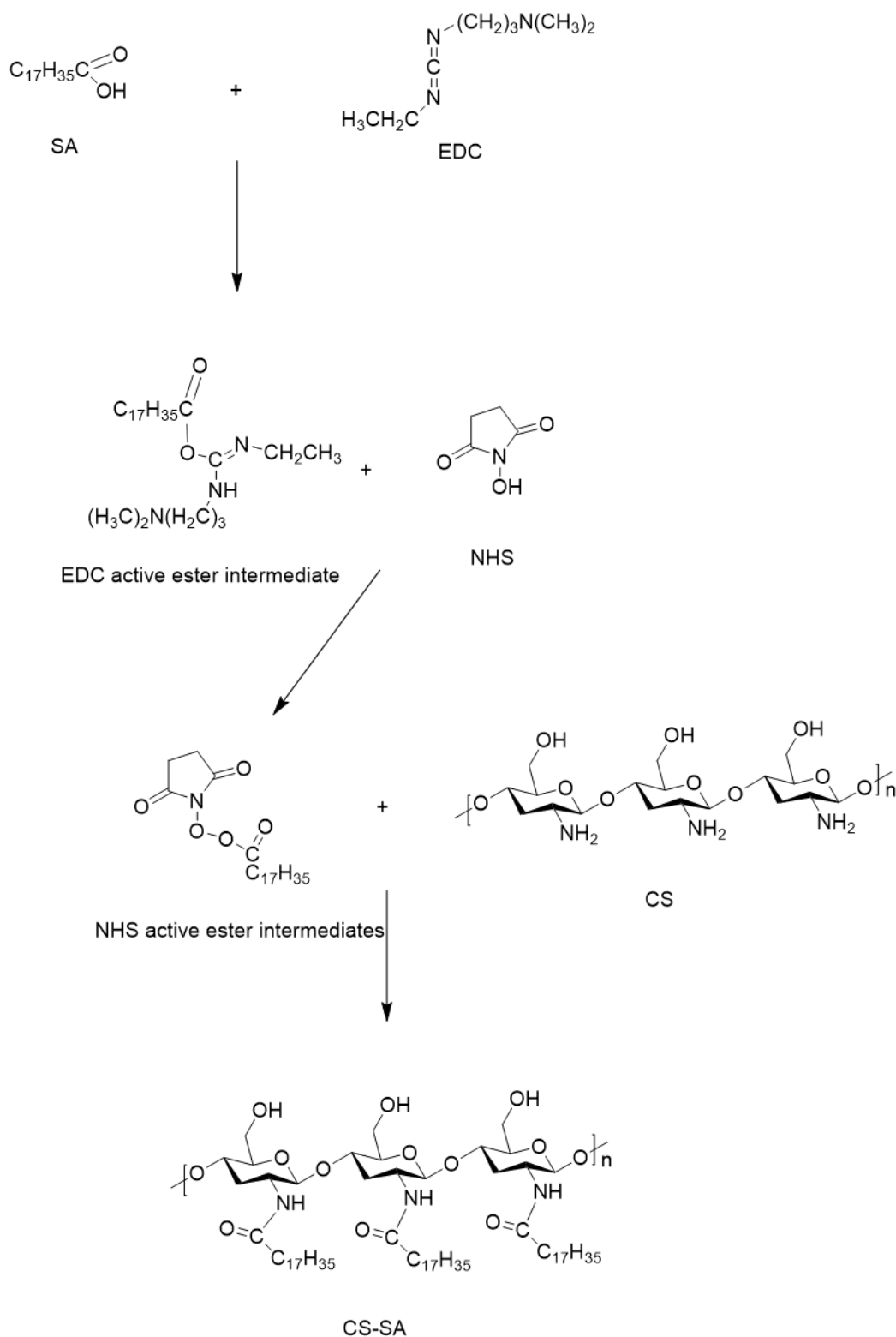


Fig. 1. Proposed formation mechanism of the CS-SA graft copolymer

In a typical synthesis for CS-8%wtSA, chitosan (CS, 2 g) was dissolved in an aqueous acetic acid solution (1 mL in 49 mL H₂O). Stearic acid (SA, 4 g) was dissolved in 46 mL ethanol and activated with EDC/NHS (0.1 g each) at 50 °C for 20 min. The activated SA was then added to the CS solution, and the reaction was continued for 14 h. To probe the structure-property relationship, variants were synthesized by 1) varying the SA mass (3 g, 5 g) at a fixed CS amount to produce CS-6%wtSA and CS-10%wtSA, and 2) using a low-DD chitosan (CS₈₅) with a fixed SA mass (4 g) to produce CS₈₅-8%wtSA. The reaction mechanism, involving EDC/NHS-facilitated amide bond formation between the SA carboxyl and CS amino groups, is shown in Fig. 1.

Preparation of Molded Pulp Specimens

The molded pulp specimens were prepared as follows. First, 12 g of bleached pulp was soaked in 1200 mL water for 20 min and subsequently disintegrated for 15 min. The slurry was then transferred to a container, where 10 g of an additive—either plain CS (4%wt), plain SA (8%wt), or a specific CS-SA copolymer—was introduced and mixed for 30 min. The fiber and additive mixture was then poured into a circular paper box mold and formed after 3 min of vacuum pumping. Finally, the formed paper boxes were hot-pressed at 180 °C for 3 min under a hot melt machine to obtain the corresponding samples. As a control, blank samples were prepared from pulp without any additives through the same process.

Characterization and Testing

A comprehensive set of characterizations was performed to elucidate the hydrophobic mechanism and application potential of the modified materials. The surface wetting properties were quantified by water contact angle (WCA, JC2000 goniometer) and Cobb value measurements. Chemical structural changes were confirmed by FTIR (Nicolet 6700, 4000 to 400 cm⁻¹) and surface composition was analyzed by XPS (Thermo Scientific Nexsa). Thermal properties were probed by TGA (TGA55) and DSC (DSC25). Morphological changes on the fiber surfaces were observed by field-emission SEM (Crossbeam 350). The resistance to liquid water penetration was tested by a 30-minute hold with 100 °C water. Furthermore, the antibacterial efficacy against *E. coli* was quantified *via* the plate counting method, and biocompatibility was evaluated by determining the cell inhibition rate of 293T cells. The surface water absorption capacity (Cobb60) of different samples was measured using the Cobb Absorbometer at 60 seconds. The work of adhesion (W_a) between water and the solid surface was calculated from the WCA using the Young-Dupré equation: $W_{LS} = \gamma_L(1 + \cos\theta)$, where W_{LS} is the work of adhesion required to separate a water droplet from the solid surface, γ_L is the surface tension of liquid water (taken as 72 mN/m at room temperature), and θ is the measured water contact angle. The subscripts L and S denote the liquid and solid phases, respectively.

RESULTS AND DISCUSSION

The fabrication process of the molded pulp and the proposed waterproofing mechanism of CS-SA are schematically illustrated in Fig. 2.

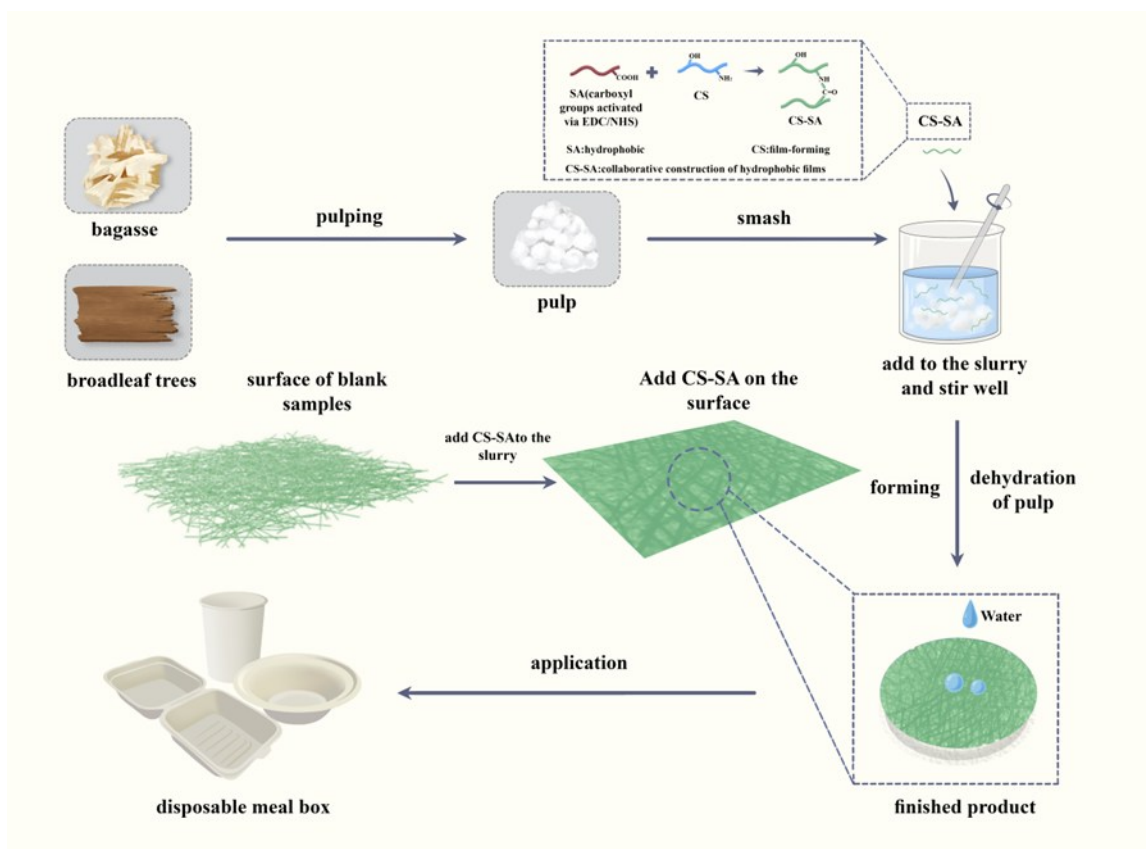


Fig. 2. Schematic illustration of the molded pulp fabrication process and the proposed waterproofing mechanism of the CS-SA copolymer

Structural Characterization

FTIR and XPS analyses were employed to verify the successful synthesis of the CS-SA graft copolymers (Fig. 3). The FTIR spectrum of CS showed its characteristic bands: a broad O-H/N-H stretch at $\sim 3382\text{ cm}^{-1}$ and peaks for residual acetamide groups at 1660 , 1550 , and 1310 cm^{-1} . The spectrum of SA was dominated by its carboxyl C=O stretch at 1700 cm^{-1} and -CH₂- stretches at $2915/2847\text{ cm}^{-1}$. In the spectra of the CS-SA products, decisive changes were observed. The SA carbonyl peak at 1700 cm^{-1} diminished significantly, while a new peak attributable to an amide C=O stretch appeared in the range 1640 to 1660 cm^{-1} . This contrast, coupled with the concurrent reduction of the CS amino band at 1580 cm^{-1} , confirms the conversion of the SA carboxyl and CS amino groups into an amide linkage. The successful grafting is further evidenced by the emergence of the characteristic SA -CH₂- stretching vibrations in all CS-SA spectra.

XPS analysis further confirmed the grafting success (Fig. 3b, Table 1). The emergence of a strong C 1s signal alongside a weakened N 1s peak in CS-SA, compared to pure CS, indicated the surface enrichment of carbonaceous species from SA. Quantitative analysis revealed a controlled, inverse relationship: increasing the SA feed ratio from 6 to 10 wt.% led to a systematic rise in carbon content (82.5% to 86.8%) and a corresponding drop in nitrogen content (2.83% to 1.43%), underscoring the reaction's controllability. The slightly higher nitrogen content in CS₈₅-8%wtSA further suggested the influence of chitosan's initial amine concentration. In summary, the collaborative FTIR and XPS results verify the covalent incorporation of SA onto CS, providing the molecular-level basis for the enhanced hydrophobicity.

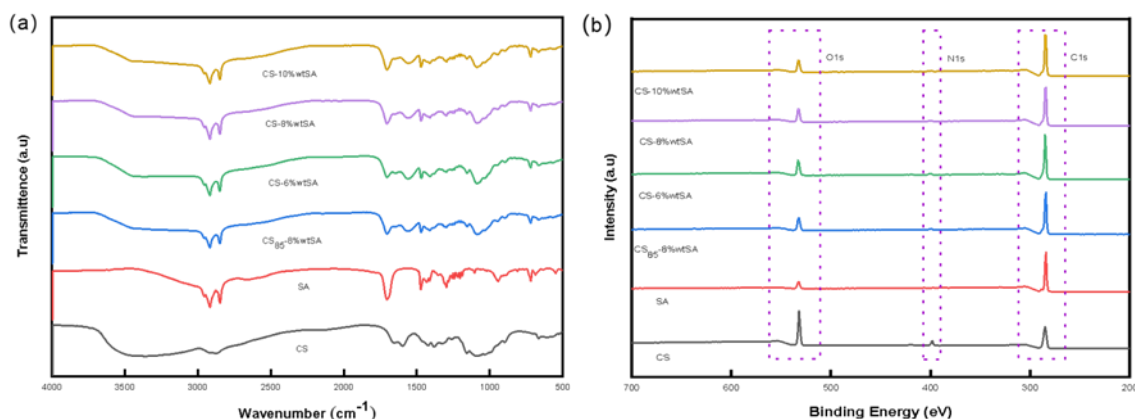


Fig. 3. (a) FTIR spectra and (b) XPS survey spectra of CS, SA, and the synthesized CS-SA graft copolymers

Table 1. Atomic Percentages (at%) of Carbon (C), Oxygen (O), and Nitrogen (N) for Chitosan (CS), Stearic Acid (SA), and the Synthesized CS-SA Graft Copolymers

Sample	C	O	N
CS	63.97	29.32	6.71
SA	91.46	8.54	0
CS ₈₅ -8%wtSA	85	13.02	1.98
CS-6%wtSA	82.53	14.64	2.83
CS-8%wtSA	84.77	13.36	1.87
CS-10%wtSA	86.77	11.81	1.43

Hydrophobic Performance (WCA and W_a)

The waterproof performance was quantified *via* water contact angle (WCA) and work of adhesion (W_a), with higher WCA and lower W_a denoting enhanced hydrophobicity (Schrader 1995). Data in Table 2 and Fig. S1 confirm that modification imparted hydrophobicity. The blank sample was instantly wetted, and pure CS remained hydrophilic (WCA=44°) due to its polar groups. The CS-8%wtSA graft copolymer yielded the best performance, with a WCA of 131° and the lowest W_a , signifying a superior water-repellent surface. All CS-SA copolymers achieved strong hydrophobicity (WCA>110°), showing that grafting facilitates the surface presentation of SA's alkyl chains.

Table 2. Water Contact Angle (WCA) and Work of Adhesion (W_a) for the Blank, CS, SA, and CS-SA Graft Copolymer Modified Molded Pulp Products

Sample	WCA (°)	W_a (J/m ²)
Blank	0	0.144
CS	44	0.12377
SA	68	0.09897
CS ₈₅ -8%wtSA	113	0.04385
CS-6%wtSA	123	0.03276
CS-8%wtSA	131	0.02477
CS-10%wtSA	119	0.03708

Performance was dependent on SA ratio and chitosan type: CS-8%wtSA

outperformed CS₈₅-8%wtSA, as higher CS deacetylation allows for greater grafting density and a more coherent film. Similarly, CS-6%wtSA had inadequate grafting, while CS-10%wtSA exhibited reduced waterproof performance due to excessive SA dosage, which led to particle precipitation after grafting reaction, increased viscosity of the copolymer solution, and molecular chain aggregation. These factors resulted in diminished film-forming properties and susceptibility to micro-defect formation.

Mechanism of Water Resistance via Cobb60 Test

The Cobb test results (Table 3) provide critical insight into the mechanism of water resistance. The blank sample's high absorptivity (1090 g/m²) originated from the hydrophilic and porous fiber network. While CS modestly improved this by forming a water-swellable physical barrier (Cobb: 871 g/m²), and SA acted as a potent hydrophobic agent (Cobb: 45.8 g/m²), their simple physical presence was suboptimal. The superior performance of the CS-SA graft copolymers unveiled a synergistic barrier mechanism. The covalent conjugation created a unified amphiphilic structure that self-assembles into a composite film on the fiber surface. The chitosan backbone provided robust adhesion and a continuous matrix, while the grafted stearic acid chains presented a dense, molecularly anchored hydrophobic canopy. This dual physical-chemical barrier was far more effective at repelling and blocking water than either component alone. The structure-property relationship was clearly demonstrated: a higher deacetylation degree in chitosan led to a denser grafted layer and lower Cobb values for a given SA ratio. Furthermore, an optimal grafting percentage was achieved (CS-8%wtSA), balancing sufficient hydrophobic coverage with the polymer's ability to form a uniform film without defects induced by excessive grafting (as in CS-10%wtSA). This demonstrates that rational molecular design is crucial for developing highly efficient waterproof pulp molded products.

The sample exhibited a minimum Cobb60 value of 12.9 g/m², which was significantly lower than that of the untreated control sample. Although the surface WCA reached 131° (indicating high surface hydrophobicity), the Cobb60 value did not approach zero. This reflects the inherent structural characteristics of pulp molded products: even after surface hydrophobic modification, micron-scale pores persist between fibers, allowing minor water absorption into the bulk phase under external water pressure or capillary action. However, the low Cobb60 value of 12.9 g/m² indicates that the CS-SA treatment not only conferred hydrophobicity to the surface but, more importantly, it established a relatively continuous water barrier within the bulk phase of the fiber network—thanks to the pulp addition strategy, which enabled CS-SA to effectively fill or seal the interconnected pores between fibers.

Table 3. Cobb60 Values of the Molded Pulp Products: Blank, CS, SA, and the Series of CS-SA Graft Copolymers

Sample	Cobb (g/m ²)
Blank	1094.32
CS	870.7
SA	45.84
CS ₈₅ -8%wtSA	20.06
CS-6%wtSA	15.11
CS-8%wtSA	12.92
CS-10%wtSA	16.71

Hot Water Resistance

The hot water resistance was tested by exposing samples to 100 °C water. The blank, CS, and SA samples failed within minutes (Table 4, Fig. S2-S3). In contrast, all CS-SA copolymers prevented leakage for the full 30-minute test duration. This result provides definitive evidence for a synergistic effect conferred by chemical grafting, highlighting a viable molecular strategy for high-performance waterproof paper. Consolidated results from WCA, W_a , Cobb, and hot water tests identified CS-8%wtSA as the optimal performer, leading to its selection for further study.

Table 4. Hot Water Resistance Time for the Blank, CS, SA, and CS-SA Graft Copolymer Modified Molded Pulp Products

Sample	Hot Water Resistance Time (min)
Blank	0
CS	2
SA	4
CS ₈₅ -8%wtSA	>30
CS-6%wtSA	>30
CS-8%wtSA	>30
CS-10%wtSA	>30

Thermal Properties (TGA)

Thermal stability was assessed *via* TGA (Fig. 4a). CS showed minor weight loss (<100 °C) from moisture evaporation, followed by major decomposition (200 to 400 °C) from backbone scission, leaving a 30 to 40% char residue. In contrast, SA degraded sharply in a single step (150 to 250 °C) due to volatilization and decomposition, leaving no residue. The CS-8%wtSA copolymer exhibited a two-stage degradation: the first (150 to 300 °C) from grafted SA chain loss, and the second (300 to 450 °C) from CS backbone degradation. Notably, CS-8%wtSA demonstrated a higher final char residue than pure CS, indicating improved thermal stability imparted by the grafted structure. This is suitable for hot-pressing pulp molded products at 180°C.

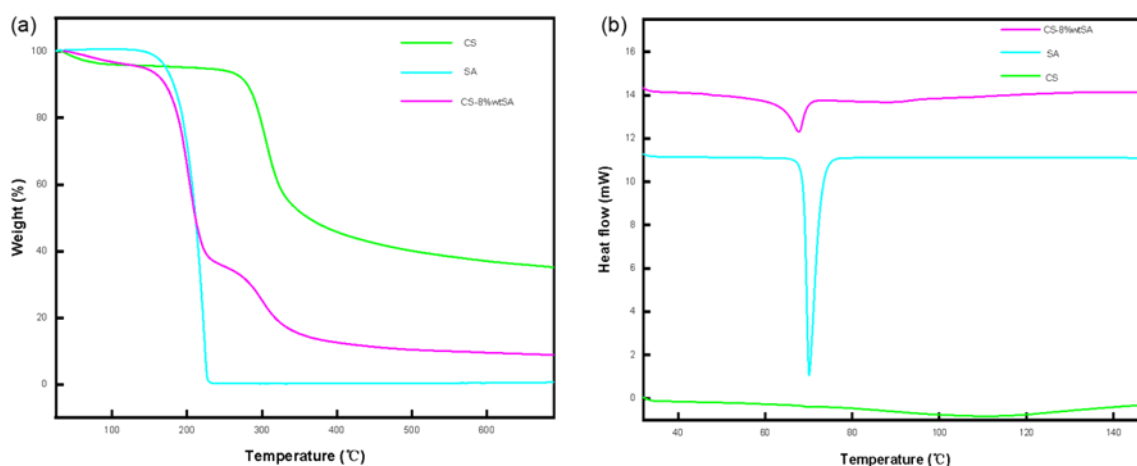


Fig. 4. Thermal analysis of CS, SA, and CS-8%wtSA: (a) TGA curves; (b) DSC curves

DSC Analysis

DSC analysis (Fig. 4b) revealed distinct thermal events. CS showed a broad endotherm at ~ 100 °C from water loss, while SA displayed a sharp melting peak at 55 to 70 °C. In contrast, the CS-8%wtSA copolymer exhibited a significantly suppressed SA melting peak, confirming that covalent grafting inhibited SA crystal formation. A shift in the CS degradation endotherm was also observed, indicating an altered decomposition pathway for the grafted polymer. This is attributed to the amphiphilic structure, which restricts SA chain mobility and perturbs the CS hydrogen-bonding network, thereby modifying the overall thermal behavior.

Morphology and Waterproof Mechanism

SEM analysis of surface and cross-sectional morphologies (Fig. 5) reveals the structural basis for the enhanced waterproofing. The blank sample exhibited an open, porous network of bare fibers (Fig. 5a-d), which promotes capillary-driven water uptake. In contrast, the CS-8%wtSA modified sample showed a continuous, dense coating that encapsulates individual fibers, seals surface pores, and consolidates the internal structure (Fig. 5e-h). This microstructural transformation effectively blocked potential pathways for liquid water penetration and prevents direct contact between water and the hydrophilic fibers, thereby suppressing hydration and swelling, and leading to the observed superior liquid resistance.

To address the issue of practical product transferability of additives, CS-SA was introduced during the suspension stirring and dispersion stage of paper fibers. Its distribution is unaffected by the porosity gradient of the final product, which constitutes the key advantage of adding CS-SA directly into the pulp over post-treatment coating. The cross-sectional morphology indicates that CS-SA had fully penetrated the pulp molding, achieving integrated waterproof performance.

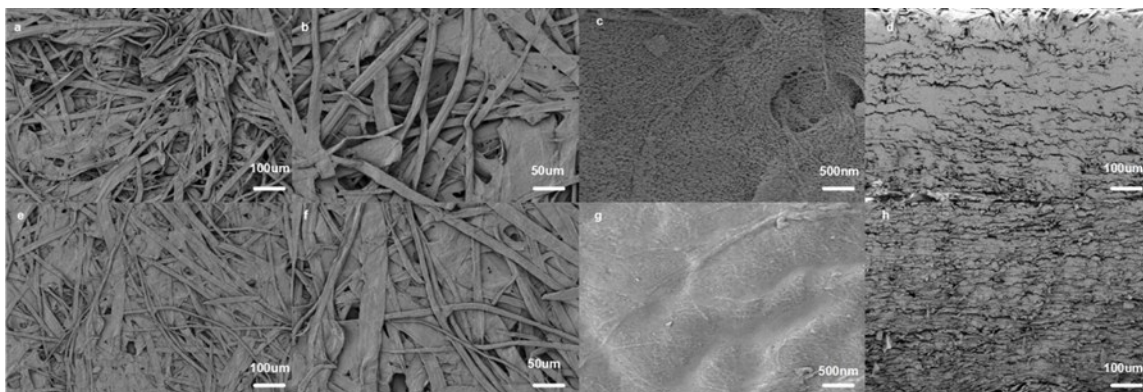


Fig. 5. Scanning electron microscopy (SEM) images of the blank sample: (a-c) surface morphology at different magnifications; (d) cross-sectional view. Corresponding images for the CS-8%wtSA modified sample: (e-g) surface morphology; (h) cross-sectional view.

Antibacterial Assessment

The antibacterial efficacy of 4%wtCS and CS-8%wtSA was assessed *via* plate counting (Fig. 6). Pure CS showed strong, concentration-dependent activity, with optimal performance at 200 $\mu\text{g/mL}$ due to effective electrostatic disruption of bacterial membranes. The CS-8%wtSA copolymer, however, exhibited moderately reduced efficacy. This is likely due to steric shielding of cationic amine groups by grafted SA chains and reduced

aqueous solubility leading to molecular aggregation, both of which hinder bacterial contact and interaction. Despite this slight decrease in antibacterial potency, the superior waterproofing conferred by CS-8%wtSA presents a valuable trade-off, establishing it as a potent dual-functional modifier for molded pulp.

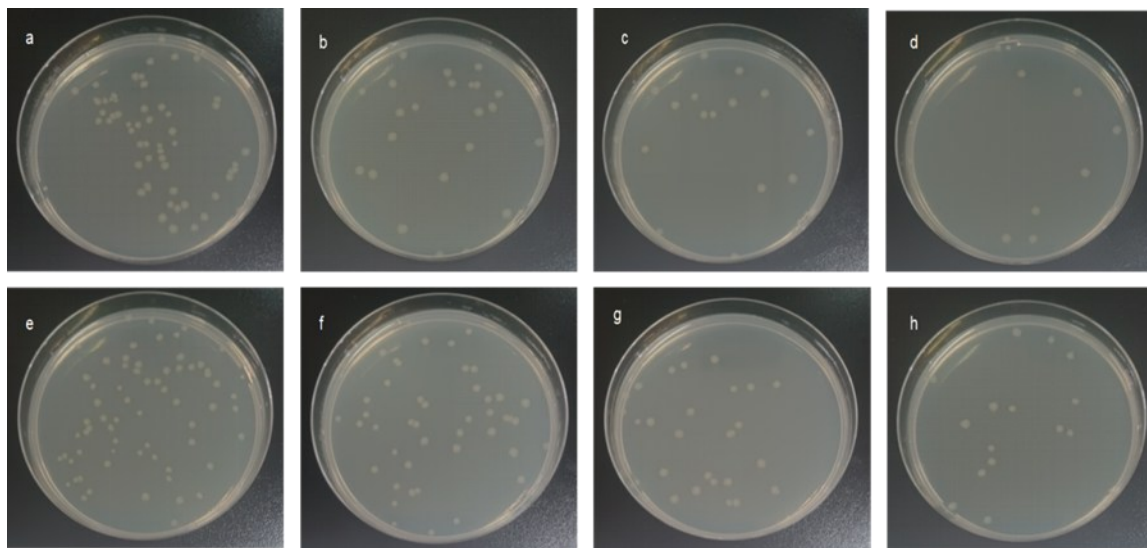


Fig. 6. Antibacterial activity of 4%wtCS and CS-8%wtSA at different concentrations. (a-d) 4%wt CS at 50, 100, 150, and 200 $\mu\text{g/mL}$, respectively. (e-h) CS-8%wtSA at 50, 100, 150, and 200 $\mu\text{g/mL}$, respectively.

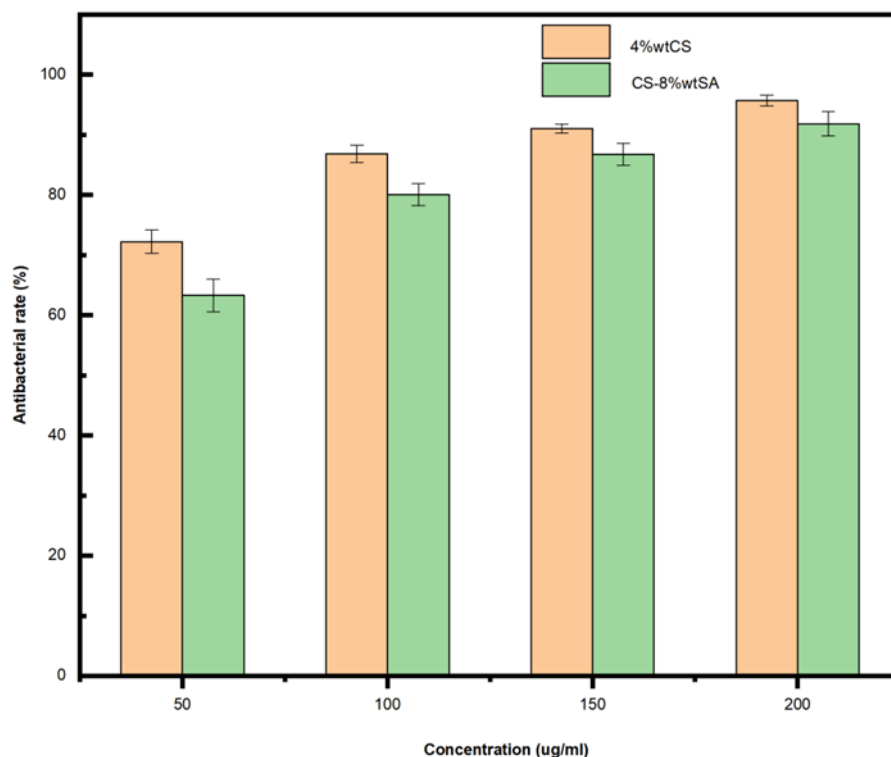


Fig. 7. Antibacterial inhibition rates of 4%wt CS and CS-8%wtSA

Analysis of Cytocompatibility

The interaction of the amphiphilic CS-8wt%SA copolymer with 293T cells was investigated to assess its biocompatibility. The results (Table 5) revealed a concentration-dependent cell inhibition profile, characterized by a plateau between 100 to 150 $\mu\text{g/mL}$. This is indicative of a saturable interaction process, followed by a renewed increase at 200 $\mu\text{g/mL}$. It is proposed that the cytotoxicity stems from the copolymer's molecular architecture. The polycationic CS backbone facilitates initial adhesion to cell membranes *via* electrostatic attraction. Concurrently, the hydrophobic SA grafts can partition into the lipid bilayer, acting as a detergent-like agent that perturbs membrane order and integrity. This biphasic mechanism—electrostatic anchoring followed by hydrophobic disruption—is characteristic of membrane-active agents and distinct from conventional chemical toxins that often interfere with specific metabolic pathways. The relatively low inhibition rates, even at high concentrations, coupled with this physicochemical mechanism, underscore its promising biocompatibility and support its potential use as a modifier for food-contact paper packaging.

Table 5. Inhibition Rate of 293T Cells by CS-8%wtSA

Concentration ($\mu\text{g/mL}$)	Inhibition Ratio (%)
20	5.94
50	14.03
100	20.82
150	21.26
200	28.34

CONCLUSIONS

1. This study successfully designed and synthesized a chitosan-stearic acid (CS-SA) graft copolymer, which functioned effectively as an eco-friendly, fluorine-free waterproofing agent when incorporated into molded pulp *via* the wet-end addition process. This addition process was found to be compatible with the papermaking process. The CS-SA modification demonstrated a significant enhancement in the water resistance of the resulting packaging material.
2. Beyond its primary waterproofing capability, the CS-SA modified pulp exhibited notable antibacterial activity while maintaining low cytotoxicity, underscoring its potential for food-contact applications. Moreover, the wet-end addition technique facilitated a homogeneous distribution and strong anchoring of the agent within the pulp matrix, yielding a modification with exceptional uniformity and durability that surpasses conventional surface coatings.
3. The verified thermal stability of the CS-SA copolymer ensures its compatibility with standard industrial hot-pressing drying operations. This work thereby validates a feasible and integrated strategy for developing high-performance, sustainable packaging by synergistically combining biodegradable materials, efficient wet-end processing, and rational graft copolymer design.

4. In the future, research on recyclability should be intensified, as the recyclability of pulp molded materials holds significant importance for the circular economy. CS-SA raw materials are all bio-based materials and can theoretically be reused along with pulp fibers. However, hydrophobic modified fibers may affect the degree of fiber hydration and subsequent sizing performance during the re-pulpification process. Subsequent systematic evaluations should assess the pulp regeneration performance of CS-SA modified materials, the degradation patterns of pulp waterproofing properties, and the cumulative environmental impacts after multiple reuse cycles, to clarify their environmental characteristics.

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Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Use of Generative AI

During the preparation of this manuscript, the authors utilized ChatGPT for assistance with grammar checking and linguistic polishing. The authors have thoroughly reviewed and edited all scientific content and take full responsibility for it.

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APPENDIX

Water Contact Angle (WCA) Measurement

The water contact angle (WCA) was measured for each sample at room temperature. Three independent measurements were performed on different locations of the sample surface, and the reported value represents the average.

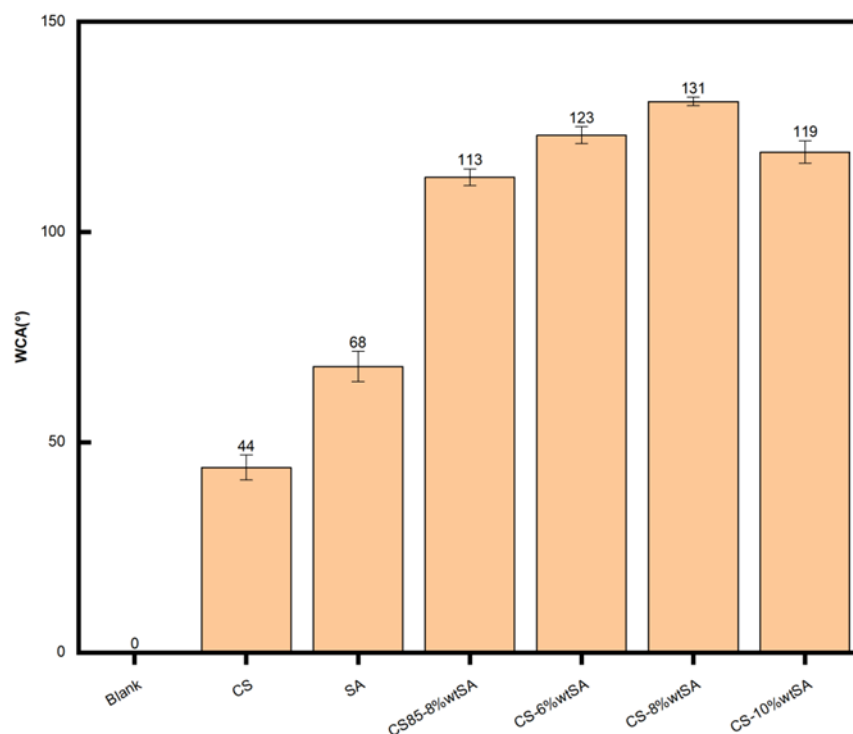


Fig. S1. Water contact angles (WCA) of the investigated samples

Assessment of Hydrothermal Stability

The resistance to hot water was assessed by adding 100 °C water into the various molded pulp samples. Phenomena such as instantaneous wetting, the timing of any leakage, and the integrity after a 30-minute duration were documented.

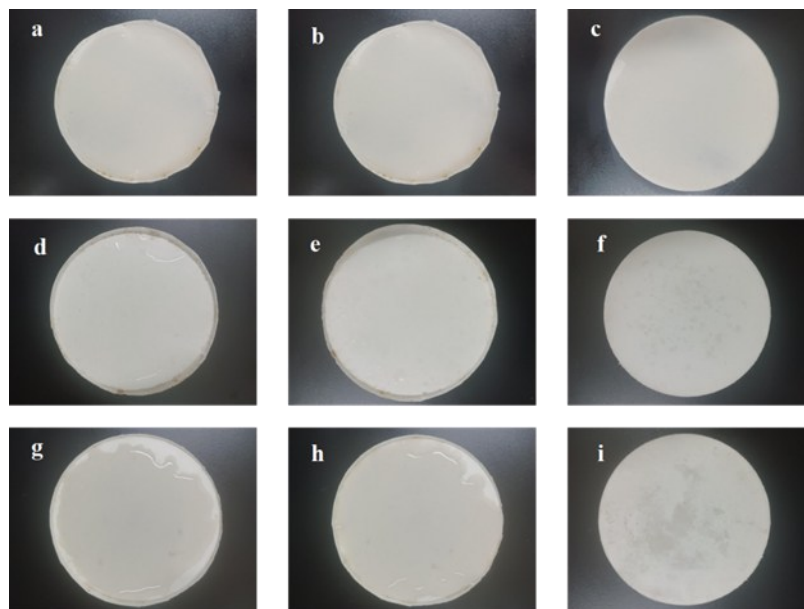


Fig. S2. Visual documentation of the waterproofing test: (a-c) blank sample; (d-f) CS-modified sample; (g-i) SA-modified sample

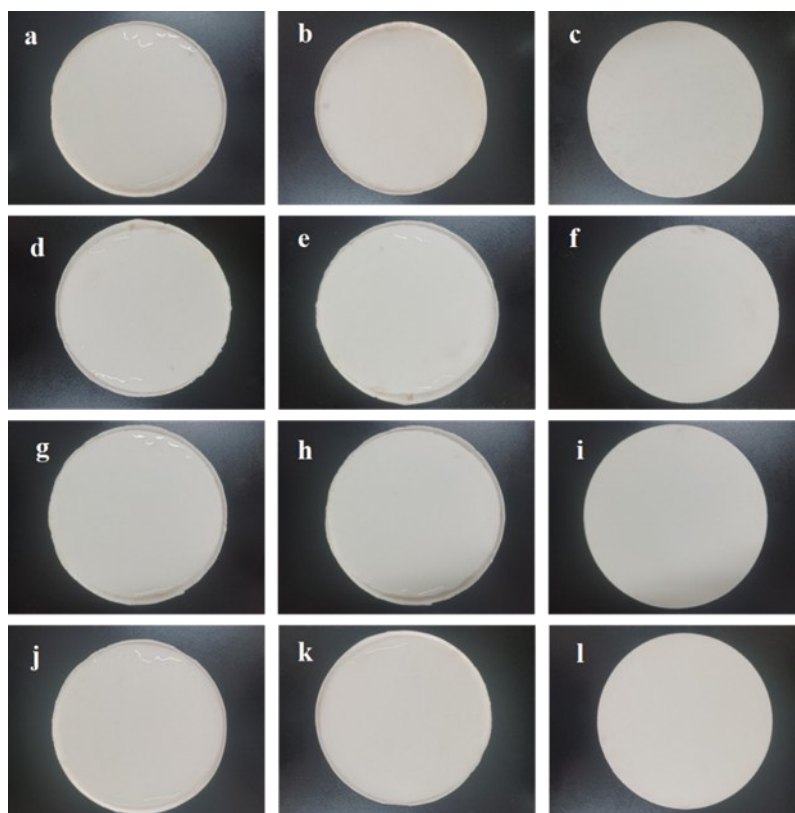


Fig. S3. Waterproofing test results for the CS-SA graft copolymers: (a-c) CS85-8%SA; (d-f) CS-6%SA; (g-i) CS-8%SA; (j-l) CS-10%SA

Antibacterial Test

The antibacterial activity was quantitatively evaluated against *E. coli* using the standard plate counting method. Briefly, the optical density (OD600) of the original

bacterial suspension was measured and adjusted to 1.0 using a spectrophotometer. The bacterial suspension was then subjected to a 10-fold serial dilution in sterile liquid medium, spanning four orders of magnitude (10^4 -fold dilution). Subsequently, 50 μL of the diluted suspension was evenly spread onto solid agar plates. The plates were incubated at 37 °C for 16 hours, after which plates containing 30 to 300 colonies were selected for counting to determine the bacterial concentration.

Antimicrobial testing methods for different sample concentrations

The antibacterial efficacy of 4% wt CS and CS-8% wt SA at concentrations of 50, 100, 150, and 200 $\mu\text{g/mL}$ was tested separately. For example, the antibacterial procedure for 4% wt CS at 50 $\mu\text{g/mL}$ concentration involves the following steps: First, weigh 50 μg of 4% wt CS and dissolve it in 1 mL of distilled water, then stir vigorously. Next, weigh 300 μL of the original bacterial solution diluted 104-fold, and thoroughly mix both solutions. Finally, 50 μL was transferred onto the solid agar plate, and four spreading beads were added for uniform coating. The uniformly coated plate was incubated at 37 °C for 16 hours.

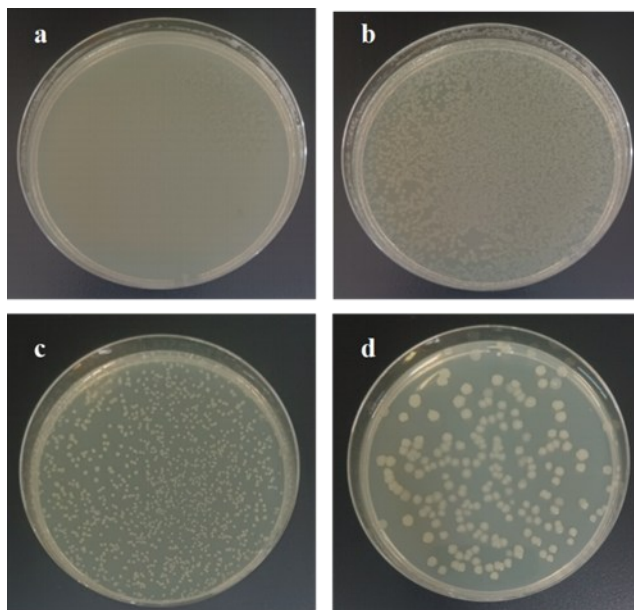


Fig. S4. Representative plates from the bacterial dilution series: (a) 10^1 dilution, (b) 10^2 dilution, (c) 10^3 dilution, (d) 10^4 dilution