

Article

Preparation, characterization, and antibacterial performance of silane-modified nanofibrillated cellulose/ZnO hybrid-reinforced poly (lactic acid) composite films

Yasheng Jiang¹, Yansheng Liu^{2,*}¹ Boston University Chobanian & Avedisian School of Medicine, Boston University, 72 East Concord Street, Boston 02118, MA, USA² Faculty of Health and Life Sciences, University of Leeds, Woodhouse Lane, LS2 9JT Leeds, UK

* Corresponding author: Yansheng Liu, Lz547957708@163.com

CITATION

Jiang Y, Liu Y. Preparation, characterization, and antibacterial performance of silane-modified nanofibrillated cellulose/ZnO hybrid-reinforced poly (lactic acid) composite films. *Journal of Polymer Science and Engineering*. 2026; 9(2): 026180009.
<https://doi.org/10.24294/jpse026180009>

ARTICLE INFO

Received: 29 April 2026

Accepted: 1 September 2026

Available online: 8 October 2026

COPYRIGHT



Copyright © 2026 by author(s).
Journal of Polymer Science and Engineering is published by EnPress Publisher, LLC. This work is licensed under the Creative Commons Attribution (CC BY) license.
<https://creativecommons.org/licenses/by/4.0/>

Abstract: PLA composite films with improved mechanical, barrier and antibacterial properties were prepared by solution casting using silane-functionalized nanofibrillated cellulose (MNFC) and chitosan-encapsulated zinc oxide nanoparticles (CS-ZnO) as dual fillers. Nanofibrillated cellulose was first soaked in an aqueous solution of zinc chloride and aluminum chloride to disrupt its hydrogen-bond network, then grafted with KH-570 (γ -methacryloyloxypropyl trimethoxysilane). This converted the cellulose from type I to type II polymorph and improved its compatibility with the hydrophobic matrix. The CS-ZnO nanohybrid was obtained by alkaline co-precipitation followed by chitosan coating, yielding a ZnO crystallite size of 18.4 nm from the Scherrer equation, with the coating limiting agglomeration. Films containing 1 to 15 wt% MNFC at a fixed CS-ZnO content of 0.25 wt% were characterized by FTIR, XRD, DSC, TGA, SEM/EDS, tensile testing, water vapor transmission measurement, and disk diffusion assay. At 5 wt% MNFC, the tensile strength reached 31.40 MPa, an increase of 113% over neat PLA, crystallinity rose from 8.67% to 35.2% and WVTR fell by 79.3% to 3.15 g/m²24 h. Inhibition zones of 18.3 mm against *E. coli* and 15.7 mm against *S. aureus* were obtained, although the mechanisms responsible for that activity were not investigated here and are discussed only with reference to the literature. MNFC therefore acts as a nucleating and reinforcing filler, while CS-ZnO supplies antibacterial activity, and the combination offers a workable route to multifunctional biodegradable packaging films.

Keywords: poly(lactic acid); nanofibrillated cellulose; zinc oxide nanoparticles; chitosan; silane modification; antibacterial; biodegradable packaging

1. Introduction

Disposable plastics continue to accumulate in terrestrial and marine environments, and the case for biodegradable materials that can take over the functions of petroleum-derived packaging has become correspondingly stronger. Poly(lactic acid) is the most commercially established member of this family and is already used at scale in food contact applications [1]. It is produced by ring-opening polymerization of lactide obtained from the fermentation of carbohydrate feedstocks such as corn starch and sugarcane; it degrades along a well-documented pathway under industrial composting conditions; and its stiffness and clarity are comparable to those of polystyrene, which makes it attractive for both rigid and flexible packaging [2,3]. Three intrinsic limitations nevertheless restrict its use in food contact applications. Commercial PLA crystallizes slowly because of its rigid backbone and the high energy barrier to chain folding, so solution-cast or melt-

quenched films are largely amorphous and typically show crystallinity below 10% against a theoretical maximum near 70% for poly(L-lactic acid), which leaves them with modest stiffness, poor heat resistance and high gas permeability [3]. Crystallinity and permeability are inversely related in PLA, and raising crystallinity from below 10% to above 30% has been reported to reduce water vapour and oxygen permeability by 50 to 80% [4]. PLA also has no intrinsic antibacterial activity, a property increasingly demanded in food contact and medical packaging where microbial contamination is a direct safety risk [1]. Addressing all three limitations within a single biodegradable matrix remains difficult [5].

Nanofibrillated cellulose is an attractive reinforcement for PLA because it is renewable, has a high aspect ratio and an axial modulus reported in the range of 100 to 150 GPa, well above that of conventional mineral fillers [6]. Its surface hydroxyl groups allow it to act as a heterogeneous nucleating agent by lowering the activation energy for PLA crystallization, and Gao and Masato reported an increase in crystallinity from 7.8% to 28.3% at 5 wt% cellulose loading [3]. The same hydroxyl-rich surface, however, drives fibre-fibre hydrogen bonding in a hydrophobic matrix and produces micron-scale bundles, which is the principal obstacle to using cellulose as a reinforcement [7]. Grafting with silane coupling agents is an established remedy, and Missoum et al. have reviewed the available chemistries for nanofibrillated cellulose [8]. Hydrolysis of the silane generates silanol groups that condense with surface hydroxyls and replace them with organofunctional groups compatible with PLA. KH-570 is a useful choice among these because its methacrylate end group carries a carbonyl that can interact with PLA carbonyls through dipole interactions, while the propyl spacer supplies chain flexibility [7,9]. Guo et al. obtained a balanced improvement in APTES-silanized cellulose nanofibre composites, with tensile strength, elongation and Young's modulus rising by 35.78%, 66.25% and 25.99% respectively at 3 wt% loading, together with a decomposition temperature of 340 °C [10]. Grafting efficiency is nevertheless limited by how many hydroxyl groups are accessible at the surface of the native type I lattice, which has prompted interest in dissolving the cellulose before functionalizing it [6].

Dissolution of cellulose in aqueous metal salt media and the accompanying type I to type II transformation have been studied primarily in the context of cellulose nanocrystals. Tong et al. showed that pretreating cellulose in NaOH/urea before hydrolysis yields type II nanocrystals with greater surface hydroxyl accessibility and better reinforcing behavior than native type I material [11]. The type II lattice has a lower inter-chain cohesion energy, which reduces the tendency of fibres to aggregate and improves wetting by organic solvents, thereby facilitating dispersion in PLA. The present work applies the same principle using a $\text{ZnCl}_2/\text{AlCl}_3$ medium, in which Zn and Al ions coordinate with cellulose hydroxyl groups, break inter-chain hydrogen bonds and swell the crystallites. After dilution and precipitation, nanofibrillated cellulose is regenerated in the type II arrangement.

Zinc oxide is among the most studied inorganic antibacterial agents, being active against both Gram-positive and Gram-negative organisms while showing low toxicity to mammals, and it is recognised as Generally Recognized as Safe by the United States Food and Drug Administration for use in food contact materials under 21 CFR [12]. Its antibacterial action is usually attributed to the release of zinc ions

that interfere with bacterial enzymes, to the photocatalytic generation of reactive oxygen species, and to electrostatic interaction between the positively charged oxide surface and the negatively charged bacterial envelope, with the relative weight of each contribution depending on particle size, surface area and whether the system is illuminated [13]. El-Habib et al. found 22 nm particles more effective than 35 and 66 nm particles against *E. coli*, *P. aeruginosa* and *S. aureus* [14], and Wei et al. described how an excess of zinc ions inhibits respiratory enzymes, promotes radical formation and damages DNA, proteins and lipids [15]. A practical difficulty in combining zinc oxide with PLA is that the oxide accelerates hydrolytic and thermal scission of PLA ester bonds at the temperatures reached during melt processing [16]. Coating the particles with chitosan addresses this in two ways, since the shell separates the oxide from the polymer chains while its amine and hydroxyl groups interact with both the oxide surface and PLA carbonyls [16]. Chitosan is itself antibacterial through the interaction of protonated amine groups with anionic cell wall components [17], and chitosan/zinc oxide combinations have been reported to give broader spectrum activity than either component alone [17]. Zheng et al. observed comparable behaviour in PLA films containing carvacrol and CNC-ZnO, which extended the shelf life of strawberries [18].

Silane-functionalized nanofibrillated cellulose and chitosan-coated zinc oxide have each been studied in PLA, but to the best of our knowledge they have not previously been combined in a single matrix, and the cellulose used in such systems has not been converted to the type II polymorph before grafting. Two features distinguish the approach taken here. The first is the two-stage treatment of the cellulose, in which dissolution in a $\text{ZnCl}_2/\text{AlCl}_3$ medium precedes silane grafting and thereby exposes hydroxyl groups that are inaccessible in the native lattice. The second is the role of the chitosan shell, which is expected to act not only as a barrier that protects PLA from oxide-catalysed chain scission but also as a compatibilizing layer between hydrophilic filler surfaces and the hydrophobic matrix, so that a single additive serves both an antibacterial and an interfacial function. PLA/MNFC/CS-ZnO films were therefore prepared by solution casting and characterized by FTIR, XRD, DSC, TGA, SEM/EDS, tensile testing, water vapour transmission measurement and disk diffusion assay, with the aim of establishing how filler content governs mechanical, barrier and antibacterial behaviour.

2. Materials and methods

2.1. Materials

Poly(lactic acid) pellets (molecular weight 100,000 to 150,000 g/mol, L-lactide content > 99%) were supplied by Zhejiang Hisun Biomaterials Co., Ltd. (Zhejiang, China). Nanofibrillated cellulose (NFC, from softwood bleached kraft pulp, fibre diameter 5 to 20 nm, length 1 to 5 μm , degree of polymerization about 800) was obtained from Zhongshan Nanofiber New Materials Co., Ltd. (Guangdong, China). Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, $\geq 99\%$), sodium hydroxide ($\geq 98\%$), chitosan (degree of deacetylation $\geq 85\%$, viscosity-average molecular weight about 200 kDa), glacial acetic acid ($\geq 99.5\%$), KH-570 (γ -methacryloxypropyltrimethoxysilane, $\geq 97\%$), zinc chloride (ZnCl_2 , $\geq 98\%$),

aluminium chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, $\geq 99\%$), dichloromethane (DCM, $\geq 99.5\%$) and absolute ethanol ($\geq 99.7\%$) were all analytical grade and were used as received. Deionized water (resistivity $\geq 18.2 \text{ M}\Omega \cdot \text{cm}$) was used throughout.

2.2. Synthesis of ZnO nanoparticles and CS-ZnO nanohybrid

ZnO nanoparticles were prepared by alkaline co-precipitation. An aqueous 0.1 M solution of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (500 mL) was heated to 60°C under magnetic stirring, and 0.2 M NaOH was added dropwise at 2 mL/min until the pH reached 10.0 ± 0.1 . The white precipitate was aged at 60°C for 2 h and collected by centrifugation (8000 rpm, 10 min). It was washed three times with deionized water and once with ethanol to remove residual acetate and sodium ions, then dried at 80°C for 12 h and calcined at 400°C for 2 h in a muffle furnace to obtain phase-pure crystalline ZnO powder.

The CS-ZnO nanohybrid was prepared as follows. Chitosan was dissolved at 1 wt% in 1% (v/v) acetic acid under stirring at 50°C for 2 h. Calcined ZnO powder was added at a CS:ZnO mass ratio of 1:2 and dispersed using a probe sonicator (300 W, 30 min, pulsed 3 s on and 1 s off). The mixture was stirred for 12 h at room temperature to allow adsorption to equilibrate, after which the pH was raised to 8.5 with dilute NaOH to precipitate the coated particles. The coated particles were collected by centrifugation, washed with deionized water, and freeze-dried before use.

2.3. Dissolution and silane modification of NFC

The dissolution medium was prepared by dissolving ZnCl_2 and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in deionized water at a molar ratio of $\text{ZnCl}_2:\text{AlCl}_3:\text{H}_2\text{O}$ of 1:0.5:10. NFC was added at 2 wt% and the suspension was stirred at 80°C for 4 h, during which the strong coordination of Zn and Al to cellulose hydroxyl groups broke the inter-chain hydrogen bonds and dissolved the fibres. The dissolved NFC was regenerated by dilution with deionized water, collected by centrifugation and washed repeatedly until residual metal was below 5 ppm for both Zn and Al by ICP-OES.

For silane modification, the regenerated NFC was dispersed in ethanol at 1 wt% by ultrasonication. KH-570 was added at 5 wt% relative to the dry mass of NFC, the pH was adjusted to 4.5 with acetic acid to promote silane hydrolysis, and the reaction was run under reflux at 70°C for 3 h. The modified NFC (MNFC) was recovered by centrifugation, washed three times with ethanol to remove unreacted silane and hydrolysis by-products, and transferred into DCM by three successive centrifugation and solvent exchange cycles followed by ultrasonication (300 W, 30 min), giving a stable MNFC/DCM dispersion at approximately 0.5 wt%.

2.4. Film preparation

PLA was dissolved in DCM at 5 wt% by stirring at room temperature for 2 h. The MNFC/DCM dispersion was combined with the PLA solution to give MNFC loadings of 1, 3, 5, 10 and 15 wt% relative to PLA, and the mixture was stirred for 1 h. CS-ZnO powder was then added at 0.25 wt% relative to PLA and dispersed by ultrasonication (200 W, 20 min). Approximately 20 mL of the casting solution was

poured onto a levelled glass plate (10 cm × 10 cm), dried for 24 h at ambient temperature and then vacuum dried at 40 °C for 12 h to remove residual solvent, giving films approximately 100 µm thick. Neat PLA and PLA/CS-ZnO (0.25 wt%) films were prepared as controls by the same procedure. The preparation workflow is shown in **Figure 1**.

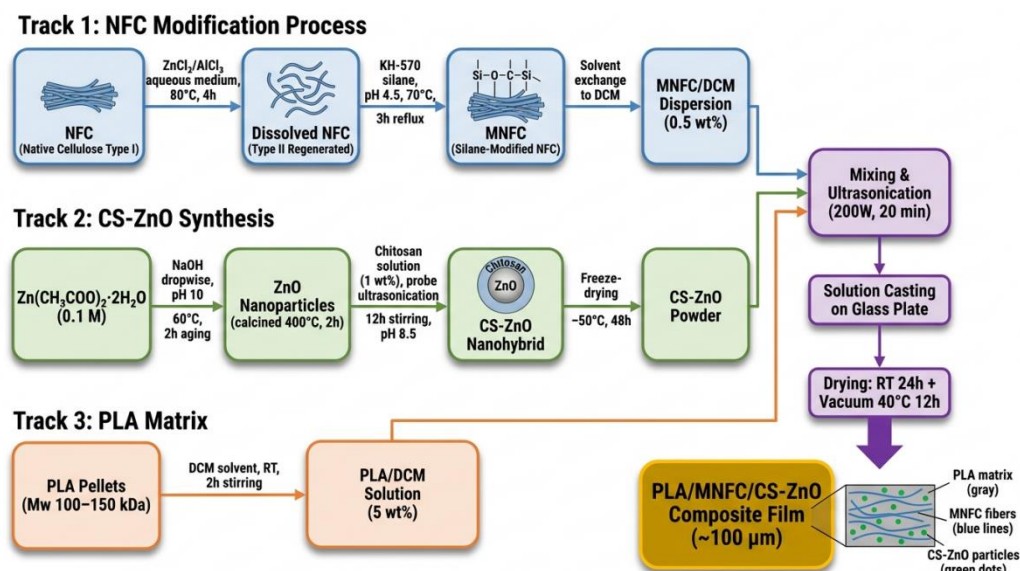


Figure 1. Preparation workflow for the PLA/MNFC/CS-ZnO composite films. Three parallel tracks, modification of NFC, synthesis of CS-ZnO and dissolution of PLA, converge at the solution casting step.

Film thickness was measured at nine points per film using a digital micrometer. The mean thickness ranged from 99.6 to 101.3 µm across formulations, with a coefficient of variation of 1.86–2.61%. Batch-to-batch reproducibility, evaluated across independently cast batches, yielded coefficients of variation below 3% for thickness, tensile strength, and WVTR, confirming that the film preparation is reproducible.

Statistical analysis was performed using OriginPro (OriginLab Corporation, Northampton, MA, USA). Mechanical ($n = 5$) and WVTR ($n = 3$) data are reported as mean $\pm$ standard deviation and were analyzed by one-way analysis of variance (ANOVA) followed by Tukey's HSD post hoc test, with statistical significance set at $p < 0.05$.

Figure 1 shows the three preparation tracks. In the cellulose track, NFC is dissolved in the $\text{ZnCl}_2/\text{AlCl}_3$ medium, grafted with KH-570 and exchanged into DCM. In the CS-ZnO track, ZnO is obtained by alkaline co-precipitation, encapsulated with chitosan and freeze-dried. In the matrix track, PLA is dissolved in DCM. The three streams are then combined, ultrasonicated and cast to give the composite films.

2.5. Characterization

Chemical structure and crystalline phase were examined by infrared spectroscopy and X-ray diffraction. FTIR spectra were recorded on a Nicolet iS50 spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) in ATR mode over

400 to 4000 cm^{-1} at a resolution of 4 cm^{-1} with 32 scans per spectrum. XRD patterns were collected on a Bruker D8 Advance diffractometer with Cu K α radiation ($\lambda = 0.15406$ nm, 40 kV, 40 mA) from 5 to 70° at 2°/min, and crystallite size was obtained from the Scherrer equation, $D = K\lambda/(\beta \cos \theta)$, with $K = 0.89$, β the full width at half maximum in radians and θ the Bragg angle.

Thermal behavior was monitored by differential scanning calorimetry and thermogravimetry, both under nitrogen at 50 mL/min. DSC was performed on a TA Instruments DSC 250, heating from 25 to 200 °C at 10 °C/min, cooling to 25 °C and reheating to 200 °C at the same rate; crystallinity was calculated from the second heating scan as $X_c (\%) = (\Delta H_m - \Delta H_{cc})/[\Delta H_m^0 \times (1 - w)] \times 100$, where $\Delta H_m^0 = 93.7$ J/g is the enthalpy of fusion of fully crystalline PLA and w is the total mass fraction of filler. Thermogravimetric analysis was carried out on a TA Instruments TGA 550 from 30 to 600 °C at 10 °C/min.

Film surfaces and cryo-fractured cross-sections were sputter-coated with 10 nm of gold and imaged on a Zeiss Sigma 300 field-emission scanning electron microscope at an accelerating voltage of 5 kV. The distributions of Si from MNFC and of Zn from CS-ZnO were mapped by energy-dispersive spectroscopy.

Mechanical and barrier performance were measured on the cast films. Tensile tests were performed on a Zwick/Roell Z010 universal testing machine at a crosshead speed of 10 mm/min using dumbbell specimens punched from the films, with a gauge length of 25 mm and a width of 4 mm; five specimens per formulation were tested, and results were reported as means and standard deviations. WVTR was measured by the desiccant method (ASTM E96) at 38 °C and 90% relative humidity, with three replicates per formulation.

Antibacterial activity was assessed against *Escherichia coli* ATCC 25922 and *Staphylococcus aureus* ATCC 6538 by agar disk diffusion. Overnight cultures were adjusted to a turbidity of 0.5 McFarland, corresponding to approximately 1×10^8 CFU/mL, and spread onto Mueller-Hinton agar plates. Film disks 6 mm in diameter were placed on the inoculated plates and incubated in the dark at 37 °C for 24 h, after which the total inhibition zone diameter, including the disk, was measured with digital callipers. Neat PLA disks served as the negative control. Each measurement was made in triplicate.

3. Results and discussion

3.1. Characterization of MNFC and CS-ZnO

3.1.1. FTIR spectroscopy

Figure 2 collects the ATR-FTIR spectra of NFC, MNFC, ZnO, chitosan, CS-ZnO and the composite films, which together track the chemical changes introduced at each stage of the preparation. Unmodified NFC in **Figure 2a** shows the features expected of cellulose, a broad and intense O-H stretching band near 3340 cm^{-1} , C-H stretching near 2892 cm^{-1} and the strong C-O-C stretching envelope of the pyranose ring below 1200 cm^{-1} [8]. After dissolution and KH-570 grafting a new band appears at 1732 cm^{-1} in the MNFC spectrum, assigned to C=O stretching of the ester linkage in the methacrylate group of the silane [7]. This band is absent from the unmodified

material and is the clearest single indication that grafting has taken place. Grafting is expected to be more extensive after the dissolution step because the type II lattice exposes hydroxyl groups that are inaccessible in the native polymorph, although NFC grafted without dissolution was not prepared here and the two cannot be compared directly. The Si-O-C stretching expected near 1100 cm^{-1} cannot be resolved from the cellulose C-O-C absorption, an overlap that is well documented in the literature on silane-functionalized cellulose [7].

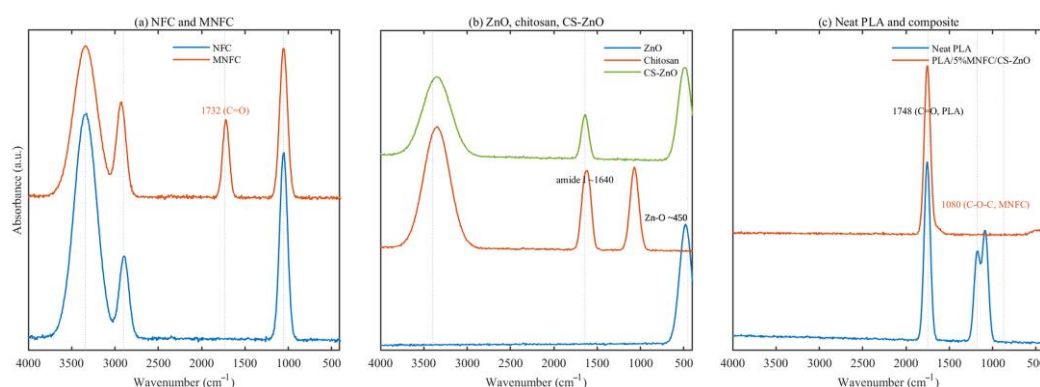


Figure 2. ATR-FTIR spectra recorded over 400 to 4000 cm^{-1} . **(a)** NFC before and after dissolution and KH-570 grafting, showing the new ester C=O band at 1732 cm^{-1} in MNFC. **(b)** ZnO, chitosan and the CS-ZnO nanohybrid, showing the Zn-O mode near 450 cm^{-1} and the amide I band near 1640 cm^{-1} retained in the hybrid. **(c)** Neat PLA and the PLA/5 wt% MNFC/0.25 wt% CS-ZnO film, in which the PLA carbonyl band remains at 1748 cm^{-1} .

Turning to the nanohybrid in **Figure 2b**, bare ZnO shows the Zn-O lattice stretching mode near 450 cm^{-1} [16]. Chitosan shows overlapping N-H and O-H stretches near 3340 cm^{-1} , amide I C=O stretch near 1640 cm^{-1} , and C-O-C stretch near 1080 cm^{-1} [16]. The CS-ZnO spectrum carries the amide I and O-H bands of the polysaccharide together with the Zn-O mode of the oxide, indicating that chitosan is retained on the particle surface after the washing steps rather than removed with the supernatant. The measurement establishes that both components are present in the recovered powder; it does not, by itself, distinguish a conformal coating from an intimate physical mixture. In the composite films of **Figure 2c**, the carbonyl stretch of PLA appears at 1748 cm^{-1} at an unchanged position, and the band near 1080 cm^{-1} is assigned to C-O-C stretch of MNFC, so no new covalent bond between PLA and the fillers is detectable after solution casting.

3.1.2. XRD analysis

Figure 3a compares the diffraction patterns of cellulose before and after treatment. Unmodified NFC shows diffraction peaks of cellulose type I at $2\theta = 14.8^\circ$, 16.5° and 22.6° , corresponding to the (1-10), (110), and (200) planes of the native parallel-chain lattice [6].

After regeneration from the $\text{ZnCl}_2/\text{AlCl}_3$ solution, the pattern instead shows reflections assignable to the (1-10)/(110) and (020) planes of cellulose type II, the antiparallel-chain polymorph that forms on regeneration from solution [11]. This transition matters because the type II lattice has a lower inter-chain cohesion energy than type I, which reduces fibre-fibre aggregation and improves wetting by organic solvents, both of which help dispersion in the PLA matrix.

surface is visibly rough, fibre bundles are apparent and the Si distribution is clearly uneven, confirming macroscopic agglomeration driven by residual hydrogen bonding between fibres [6]. EDS mapping of Zn in the 5 wt% MNFC/0.25 wt% CS-ZnO film shows a uniform fine-scale distribution with no macroscopic aggregates, which is attributed to steric stabilization by the chitosan shell.

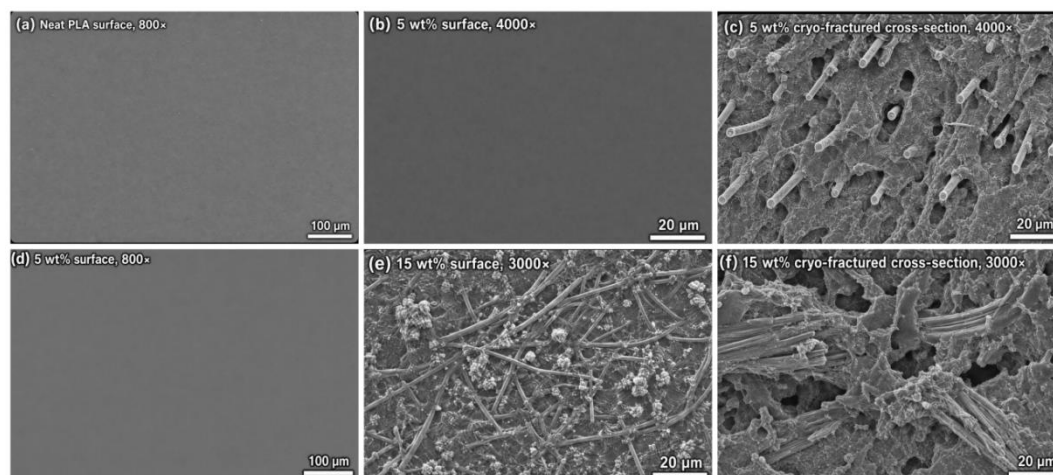


Figure 4. SEM micrographs of film surfaces and cryo-fractured cross-sections, with the magnification marked on each panel. (a) Neat PLA surface. (b) Surface of the 5 wt% MNFC film at higher magnification. (c) Cross-section of the 5 wt% MNFC film, showing fibre pull-out and matrix deformation. (d) Surface of the 5 wt% MNFC film, recorded at the same magnification as (a) so that the two can be compared directly. (e) Surface of the 15 wt% MNFC film, showing fibre bundles. (f) Cross-section of the 15 wt% MNFC film. The absence of resolvable features in (a), (b) and (d) is itself the result, since it shows that no aggregates or surface defects are present at these loadings. All films other than neat PLA contain 0.25 wt% CS-ZnO. Scale bars are marked in each panel.

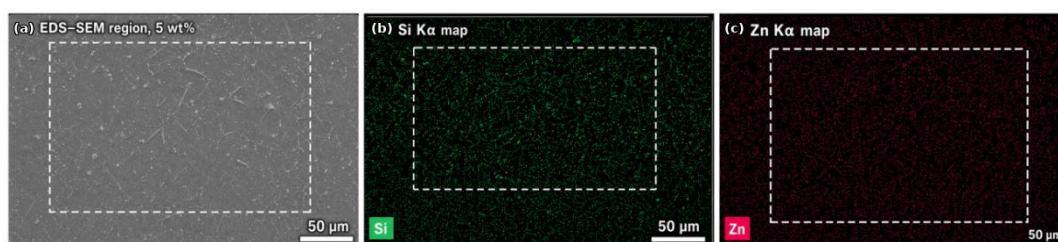


Figure 5. EDS elemental mapping of the PLA/5 wt% MNFC/0.25 wt% CS-ZnO film. (a) SEM image of the mapped region. (b) Si K α map, indicating the distribution of MNFC. (c) Zn K α map, indicating the distribution of CS-ZnO. Scale bars 50 μ m.

3.2.2. XRD analysis of composite films

The pattern of the optimized film in **Figure 3c** shows that PLA crystallizes in the presence of MNFC. Reflections appear at $2\theta = 14.8^\circ$, 16.8° and 19.2° , assigned to the (010), (110)/(200) and (203) planes of the α form [6]. The (010) reflection is the diagnostic one, since it is absent from poorly crystalline PLA, and its presence here is consistent with the crystallinity of 35.2% obtained by DSC for the same formulation. Reflections of ZnO are also detectable at 2θ near 36.3° and 56.6° , which confirms that the crystalline oxide phase survives solution casting and drying and that the chitosan coating does not amorphise the core. Diffraction patterns were

not recorded for the other loadings, so the dependence of crystallinity on MNFC content is established below from DSC rather than from diffraction.

3.2.3. Thermal analysis

DSC quantifies the films' crystallization behavior. The crystallinity and cold crystallization temperature are plotted against MNFC loading in **Figure 6**. The corresponding thermograms are shown in **Figure 7**, with the second heating scans in panel (a) and the cooling scans in panel (b). The parameters taken from the second heating scans are collected in **Table 1**. Neat PLA shows a glass transition at 54.3 °C, a cold crystallization exotherm at 108.0 °C, a melting endotherm with a low-temperature shoulder at 157.2 °C and a maximum at 164.5 °C, the shape expected for the melt-recrystallization sequence of the α' and α forms, and a crystallinity of only 8.67% [3]. The shoulder disappears once MNFC is present, and the endotherm becomes a single symmetric peak near 163 °C, which indicating that nucleation by MNFC allows the α form to develop directly on cooling without passing through the α' phase. The glass transition rises slightly with MNFC content, reaching 55.5 °C at 5 wt%, consistent with restricted segmental mobility at the filler interface. The cold crystallization temperature falls from 108.0 °C in neat PLA to 95.8 °C at 5 wt% MNFC, and ΔH_{cc} drops sharply, showing that a much larger fraction of the crystallization now occurs during cooling rather than on reheating, which is the clearest evidence of heterogeneous nucleation. Crystallinity peaks at 35.2% for the 5 wt% MNFC/0.25 wt% CS-ZnO film, 4.1 times that of neat PLA, and declines at higher loadings, where agglomeration reduces the effective nucleating surface and hinders chain mobility. A separate series without CS-ZnO was not prepared, so the individual contribution of the oxide to nucleation cannot be isolated from the present data.

Table 1. DSC parameters of the PLA composite films taken from the second heating scan.

Sample	T _g (°C)	T _{cc} (°C)	T _{m1} (°C)	T _{m2} (°C)	ΔH_{cc} (J/g)	ΔH_m (J/g)	X _c (%)
Neat PLA	54.3	108.0	157.2	164.5	24.57	32.69	8.67
PLA/CS-ZnO (0.25 wt%)	54.5	105.3		163.8	18.42	33.15	15.73
PLA/1 wt%							
MNFC/CS- ZnO	55.1	95.2		163.0	6.08	33.85	30.54
PLA/3 wt%							
MNFC/CS- ZnO	55.3	94.1		163.2	5.71	34.62	32.41
PLA/5 wt%							
MNFC/CS- ZnO	55.5	95.8		163.4	5.63	34.91	35.20
PLA/10 wt%							
MNFC/CS- ZnO	55.4	97.6		163.3	4.52	33.51	33.87
PLA/15 wt%							
MNFC/CS- ZnO	54.8	98.8		163.6	6.87	28.63	26.94

Figure 6 shows both the nucleating efficiency of the filler and the loading window over which it operates.

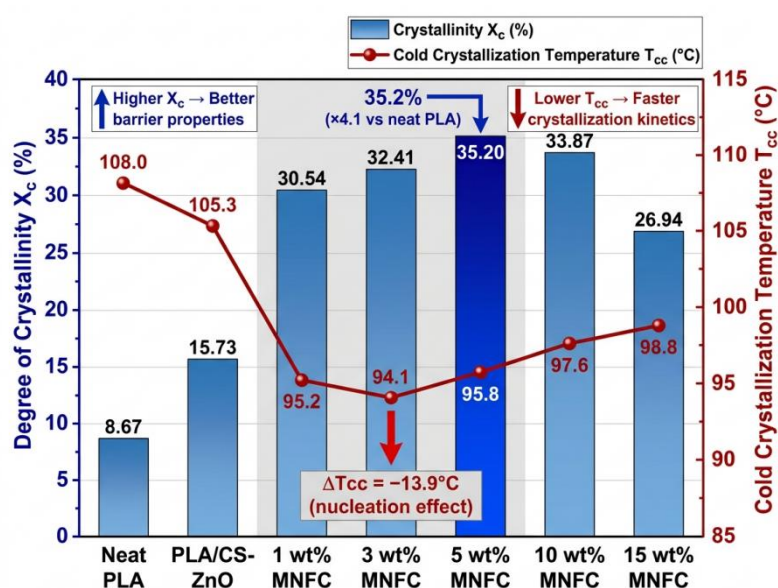


Figure 6. Crystallinity (X_c , left axis, bars) and cold crystallization temperature (T_{cc} , right axis, line) as a function of MNFC loading in the PLA/MNFC/CS-ZnO films, all of which contain 0.25 wt% CS-ZnO.

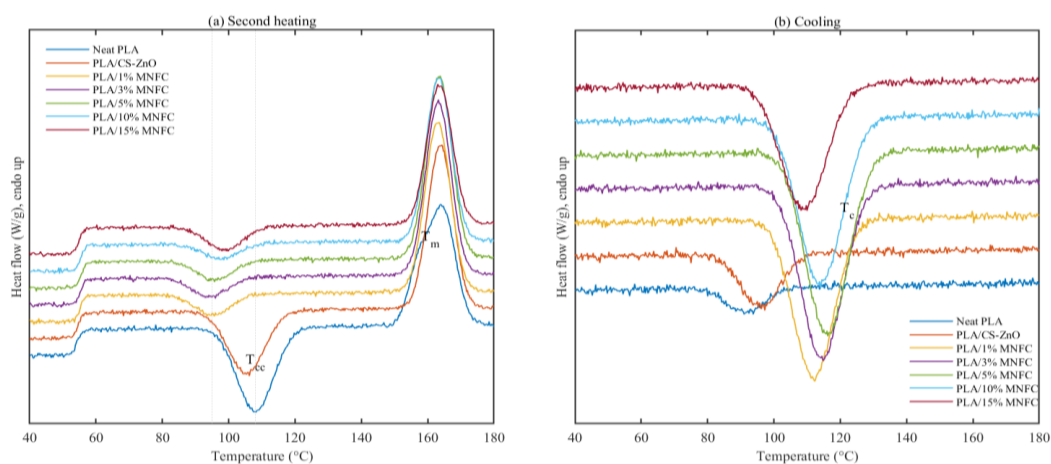


Figure 7. DSC thermograms of neat PLA and the composite films. **(a)** Second heating scan, in which the low-temperature shoulder on the melting endotherm of neat PLA is absent once MNFC is present. **(b)** Cooling scan.

As **Figure 6** shows, crystallinity rises from 8.67% for neat PLA to 30.54% with only 1 wt% MNFC, which confirms the efficiency of MNFC as a heterogeneous nucleating agent. The maximum of 35.2% is reached at the optimum loading of 5 wt%, a 4.1-fold increase over neat PLA. Cold crystallization temperature falls from 108.0 °C for neat PLA to a minimum of 94.1 °C at 3 wt% and stands at 95.8 °C at the optimum 5 wt% loading, which quantifies the acceleration of crystallization produced by the added nucleation sites.

The mass-loss and derivative curves are presented in **Figure 8**. Neat PLA begins to lose mass at $T_{5\%} = 345.2$ °C with the maximum rate at $T_{max} = 373.4$ °C, consistent with the β -elimination pathway generally accepted for PLA degradation [6]. Adding MNFC lowers $T_{5\%}$ substantially, to approximately 307 °C at 5 wt%, a reduction of some 38 °C that deserves comment rather than being treated as incidental. Two contributions are plausible. Cellulose itself begins to decompose

near 210 °C, so the filler introduces a population of thermally labile sites well below the onset for the matrix, and **Figure 8** shows the onset moving progressively lower as filler content rises. In addition, traces of Zn and Al retained from the dissolution medium may catalyse ester bond scission, and although ICP-OES showed residual metal below 5 ppm, this cannot be ruled out on the present evidence since the two contributions were not separated experimentally. Doing so would require TGA of the regenerated NFC before and after exhaustive metal removal, which was not attempted here. The practical consequence is limited for the intended application, since T5% remains above 300 °C for every formulation, well above the temperatures encountered in solution casting and far above any food packaging service condition. It would matter considerably more for melt processing, where residence at 180 to 200 °C is unavoidable and where a reduced degradation onset narrows the usable processing window. Any extension of this system to extrusion or injection moulding should therefore be preceded by a study of melt stability rather than assuming that the solution-cast results transfer. The PLA/CS-ZnO film containing 0.25 wt% of the nanohybrid and no MNFC decomposes over essentially the same range as neat PLA, with no measurable reduction in onset temperature. Bare ZnO has been reported to accelerate ester scission at comparable loadings, so the absence of any such shift here is consistent with the chitosan shell acting as a barrier between the oxide and the polymer chains, although the uncoated oxide was not tested in this system and the comparison therefore rests on the literature [16]. The residual mass at 600 °C increases with filler content, as expected from the inorganic residue left by the silane grafts and the oxide.

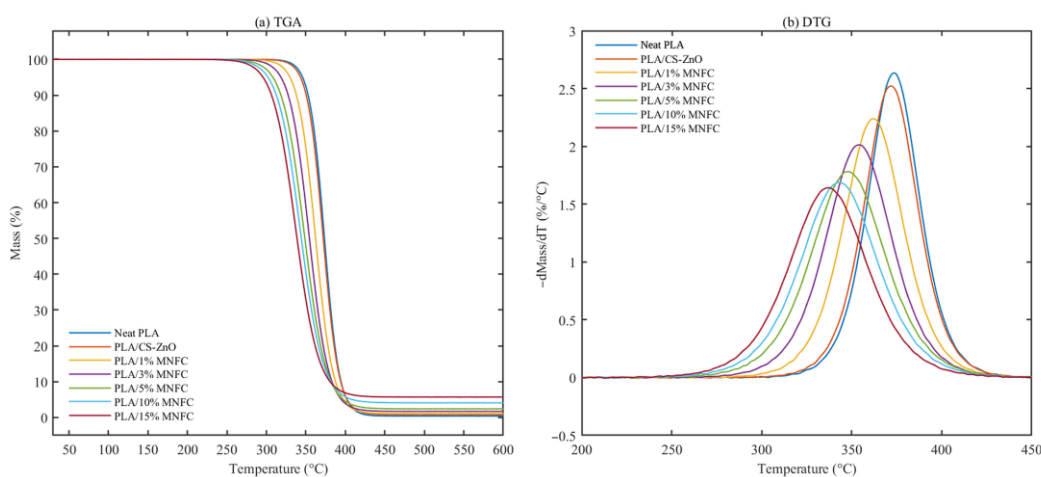


Figure 8. Thermal decomposition under nitrogen. **(a)** TGA mass-loss curves. **(b)** DTG curves. The onset temperature falls with MNFC content while all formulations remain stable above 300 °C.

3.2.4. Mechanical properties

Table 2 and **Figure 9** summarize the tensile results for all formulations. Neat PLA has a tensile strength of 14.72 MPa and a strain at break of 10.32%, reflecting the brittleness of a poorly crystalline film. This value is well below the 40 to 70 MPa typically reported for PLA film, which refers to melt-extruded or oriented material; solvent casting from dichloromethane yields an unoriented, low-crystallinity film with correspondingly low absolute strength. All comparisons below are therefore

between films produced by the same route. Adding 0.25 wt % CS- ZnO alone raises tensile strength to 18.90 MPa, an increase of 28.4%, and elongation to 13.10%, which can be attributed to the compatibilizing action of chitosan at the interface, together with the rise in crystallinity from 8.67 to 15.73%. Tensile strength then increases progressively with MNFC content to a maximum of 31.40 MPa at 5 wt %, 113% above neat PLA. Three contributions account for this. The high axial stiffness of the fibres permits efficient load transfer from the matrix, provided interfacial adhesion is adequate, which KH- 570 grafting supplies. The fourfold increase in crystallinity at 5 wt % produces a denser, more interconnected crystalline network that resists deformation and raises fracture energy. Physical entanglement of the fibres also constrains chain mobility independently of crystallinity [6]. Films containing MNFC alone were not prepared, so the separate contribution of CS- ZnO to strength at a given MNFC loading cannot be quantified from these data, although the increase obtained with CS- ZnO alone indicates that the chitosan- mediated interface does contribute [16]. At 10 wt % MNFC, the tensile strength falls to 27.80 MPa, even though crystallinity remains above 33%, which is attributable to stress concentrations at fibre aggregates acting as crack initiation sites. At 15 wt %, the films were too brittle for reliable tensile measurement, consistent with the severe agglomeration seen by SEM.

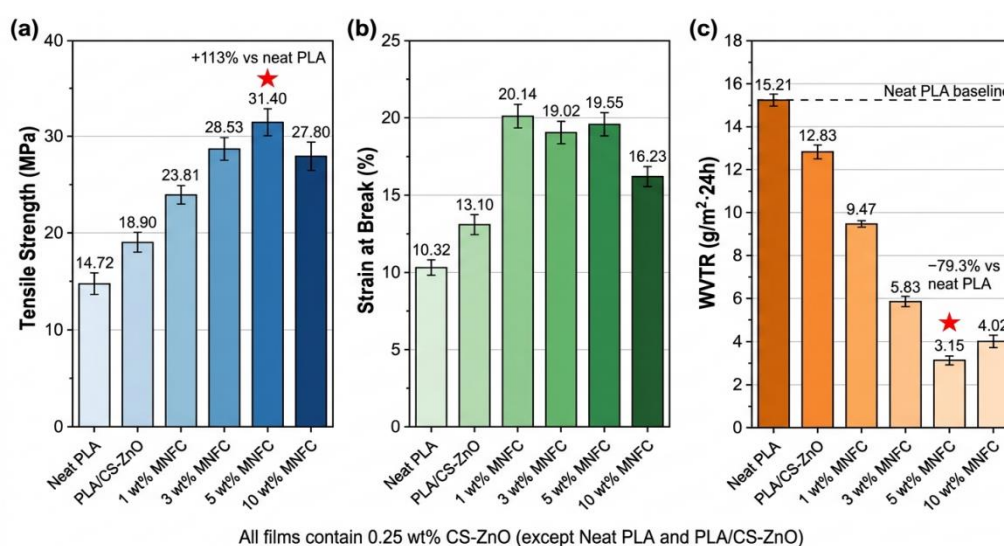


Figure 9. (a) Tensile strength, (b) strain at break and (c) water vapour transmission rate of the PLA composite films as a function of MNFC loading. All dual-filler films contain 0.25 wt% CS-ZnO. Error bars are standard deviations, with $n = 5$ for tensile properties and $n = 3$ for WVTR. Red stars denote the optimal composition (5 wt% MNFC), which simultaneously achieves the highest tensile strength (+113% over neat PLA) and the lowest WVTR (−79.3% over neat PLA).

The strain at break data show pronounced toughening at low to moderate MNFC loadings. Elongation almost doubles from 10.32% for neat PLA to 20.14% at 1 wt % MNFC, as the fibres bridge incipient cracks and absorb energy through pull- out and matrix deformation. The effect diminishes as loading increases and aggregates begin to act as stress concentrators, and elongation falls to 16.23% at 10 wt %. The combination of 31.40 MPa and 19.1955% at 5 wt % MNFC represents a

balance of stiffness and toughness that is not often achieved simultaneously in PLA nanocomposites.

Table 2. Tensile properties and water vapour transmission rate of the PLA composite films.

Sample	Tensile strength(MPa)	Strain at break(%)	WVTR(g/m ² 24h)
Neat PLA	14.72 ± 0.8 ^e	10.32 ± 0.6 ^d	15.21 ± 0.4 ^a
PLA/CS-ZnO(0.25 wt%)	18.90 ± 1.1 ^d	13.10 ± 0.7 ^c	12.83 ± 0.5 ^b
PLA/1 wt%MNFC/CS-ZnO	23.81 ± 1.3 ^c	20.14 ± 1.1 ^a	9.47 ± 0.3 ^c
PLA/3 wt%MNFC/CS-ZnO	28.53 ± 1.5 ^b	19.02 ± 0.9 ^a	5.83 ± 0.4 ^d
PLA/5 wt%MNFC/CS-ZnO	31.40 ± 1.4 ^a	19.55 ± 1.0 ^a	3.15 ± 0.2 ^e
PLA/10 wt%MNFC/CS-ZnO	27.80 ± 1.6 ^b	16.23 ± 0.8 ^b	4.02 ± 0.3 ^e

Values are expressed as mean ± standard deviation ($n = 5$ for mechanical properties, $n = 3$ for WVTR). Within each column, values followed by different superscript letters differ significantly ($p < 0.05$, one-way ANOVA with Tukey's HSD test).

As **Figure 9** shows, tensile strength and WVTR move in opposite directions with MNFC loading and both reach their optimum at 5 wt%. That the two optima coincide indicates that the crystallinity increase induced by MNFC is the common driver, since crystalline domains resist mechanical deformation and obstruct water vapour diffusion at the same time.

3.2.5. Water vapor barrier properties

Neat PLA has a WVTR of 15.21 g/m²24 h, which reflects the permeability of a largely amorphous microstructure. CS-ZnO alone reduces this to 12.83 g/m²24 h, a decrease of 15.6%. At a loading of 0.25 wt% the particles can contribute little tortuosity, so this reduction is attributed mainly to the accompanying rise in crystallinity from 8.67 to 15.73%. MNFC produces a far larger effect, and WVTR falls to 3.15 g/m²24 h at 5 wt%, 79.3% below neat PLA. Two mechanisms act together, as illustrated in **Figure 10**. The high aspect ratio of the fibres forces water vapour to travel around impermeable obstacles and lengthens the effective diffusion path [21]. At the same time, the 4.1-fold increase in crystallinity reduces the amorphous fraction available for sorption and diffusion, since crystalline PLA is effectively impermeable to small molecules [4]. WVTR rises slightly at 10 wt% MNFC, to 4.02 g/m²24 h. This value does not differ significantly from the 5 wt% result by Tukey HSD, so the change should be read as the loss of further improvement rather than as a measurable deterioration, and it is consistent with the lower crystallinity and the additional free volume associated with partial agglomeration at that loading. No value is reported at 15 wt%, since films at that loading were too brittle to be mounted in the permeation cell without damage.

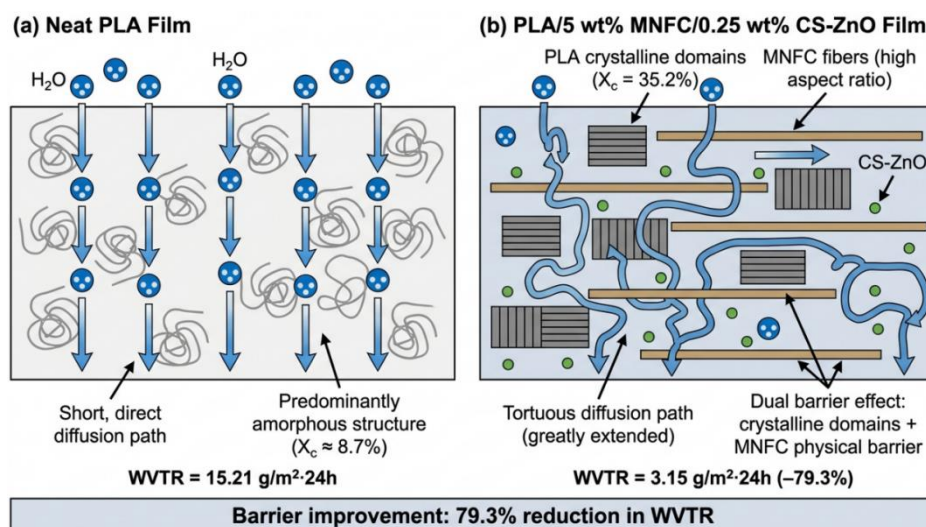


Figure 10. Water vapour diffusion pathways in (a) a neat PLA film and (b) the PLA/5 wt% MNFC/0.25 wt% CS-ZnO film, illustrating the combined effect of impermeable crystalline domains and MNFC-induced tortuosity.

Figure 10 contrasts the two situations. In neat PLA (panel a) water vapour moves through the amorphous matrix along relatively direct paths. In the composite film (panel b) the high aspect ratio fibres and the crystalline PLA domains together impose a much longer and more convoluted route, which accounts for the 79.3% reduction in WVTR. This dual mechanism follows the tortuous path model developed for PLA/clay nanocomposites, which accounts quantitatively for the combined influence of crystallinity and filler aspect ratio on water vapour permeability [4].

3.3. Antibacterial activity

Neat PLA films produced no inhibition zone against either test organism, which confirms that the matrix itself carries no intrinsic antimicrobial activity. Films containing 0.25 wt% CS-ZnO gave inhibition zones of 14.2 ± 0.8 mm against *E. coli* and 12.1 ± 0.6 mm against *S. aureus*, so a loading well below 1 wt% is already sufficient to impart measurable activity. The optimized PLA/5 wt% MNFC/0.25 wt% CS-ZnO film gave the largest zones, 18.3 ± 1.1 mm and 15.7 ± 0.9 mm respectively. The larger zones obtained when MNFC is present are consistent with a more uniform distribution of CS-ZnO in the denser and more crystalline matrix.

The pathways summarised in **Figure 11** are drawn from the published literature on ZnO and chitosan rather than established by the measurements reported here. Zinc ions released from ZnO surfaces are known to bind thiol groups in bacterial respiratory enzymes and to disrupt active transmembrane transport and amino acid metabolism [15]. ZnO is a direct bandgap semiconductor with a gap near 3.3 eV and can generate reactive oxygen species photocatalytically, but that route requires illumination and is unlikely to contribute appreciably under the conditions used here, since the inoculated plates were held in the dark at 37 °C for 24 h [13]. The positively charged ZnO surface can associate with the negatively charged bacterial envelope and cause depolarization, and the protonated amine groups of the chitosan shell can interact with anionic wall components in a comparable way [17]. Larger zones were observed against *E. coli* than against *S. aureus* for every formulation.

This difference is commonly ascribed to envelope architecture and to the size of the ZnO crystallites [14], although reports on ZnO are not unanimous about its direction, and the present measurements do not resolve the question.

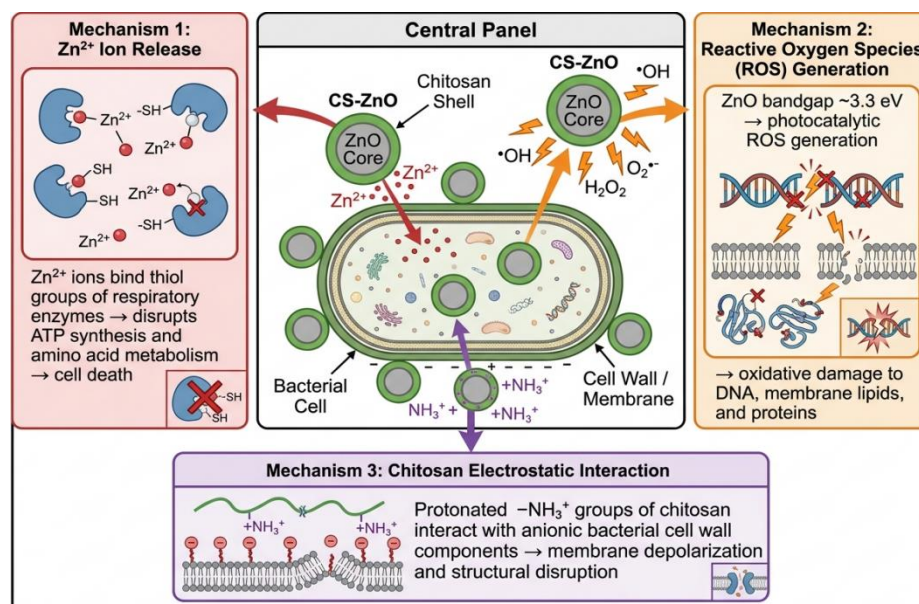


Figure 11. Proposed antibacterial pathways of CS-ZnO compiled from the published literature: (1) release of Zn ions and interference with respiratory enzyme function, (2) photocatalytic generation of reactive oxygen species, and (3) electrostatic interaction of the ZnO surface and of protonated chitosan amine groups with the bacterial envelope. None of these pathways was measured in the present study and the scheme is included for orientation only.

No measurement in this study directly addresses any of these pathways. Zinc release from the films was not quantified, reactive oxygen species were not detected, the zeta potentials of the fillers and of the film surfaces were not recorded, and bacterial morphology after contact with the films was not imaged. A disk diffusion assay reports only the net outcome of whatever combination of pathways is active, so the data presented here cannot apportion the observed activity among them. One inference is nevertheless available from the assay itself. An inhibition zone can form only if an active species migrates out of the film and into the surrounding agar, since the fillers are immobilised in the matrix and cannot themselves diffuse. The zones observed here therefore indicate that a soluble species is released, which is consistent with the zinc release pathway, although the assay identifies neither the species nor the quantity involved. It also follows that disk diffusion measures a different property from the one that governs performance in packaging, where the film acts by contact with the food surface rather than by releasing an agent into a gel. A contact assay such as ISO 22196 would therefore be the more informative test for this application. The two fillers likewise cannot be said to act synergistically against bacteria, since no antibacterial control containing MNFC alone was tested. Quantitative measurement of zinc release into food simulants, of oxidative stress markers, and of membrane integrity is required before any of these mechanisms can be assigned to this system, and such work is planned as a continuation of the study.

3.4. Structure-property relationships

The characterization data indicate why the 5 wt% MNFC/0.25 wt% CS-ZnO formulation outperforms the others. The two-stage treatment of the cellulose, dissolution followed by KH-570 grafting, is what makes MNFC an effective nucleating and reinforcing agent in a hydrophobic matrix. Grafting on the native type I lattice is limited by the accessibility of surface hydroxyl groups, and silanized type I cellulose has been reported to remain hydrophilic enough to aggregate in organic media [8]. The corresponding films were not prepared here, so this comparison rests on the literature rather than on the present measurements. The type II polymorph, with its antiparallel chain arrangement and lower inter-chain cohesion energy, offers a more accessible surface for silane condensation and a more compatible interface with PLA [11].

The nucleating efficiency achieved here is high, a 4.1-fold increase in crystallinity at 5 wt% loading against the best comparable literature value of 3.6-fold at 10 wt% in a similar system [6]. The greater surface area and the improved accessibility of hydroxyl groups in type II MNFC provide a reasonable explanation. The increase in crystallinity in turn improves both mechanical and barrier behaviour, since a higher density of crystallites resists deformation and leaves fewer amorphous domains through which water vapour can diffuse. The relationship between crystallinity and WVTR found here is consistent with the tortuous path model of Sharafi Zamir et al., who reported a 60 to 70% reduction in water vapour permeability when PLA crystallinity rose from 10 to 35% in PLA/starch nanocrystal composites [4].

CS-ZnO at 0.25 wt% contributes to the composite in ways that go beyond its antibacterial role. The chitosan shell acts as a compatibilizer at the particle/matrix interface, improving dispersion and reducing the oxide-catalysed chain scission reported for bare ZnO at similar loadings [16]. Adding CS-ZnO alone to PLA raises crystallinity from 8.67 to 15.73% and tensile strength from 14.72 to 18.90 MPa, which shows that the oxide surfaces nucleate the matrix and that the interface transfers stress even in the absence of MNFC [3]. How much of the performance of the dual-filler films is attributable to CS-ZnO at a fixed MNFC content cannot be established here, since the corresponding single-filler series was not prepared.

With respect to the antibacterial performance of the optimized film, which exhibits inhibition zones of 18.3 mm against *E. coli* and 15.7 mm against *S. aureus*, the result should be assessed against the antimicrobial filler loading required to achieve it. Zheng et al. [18] reported substantially larger inhibition zones (approximately 49 mm against *E. coli* and 50 mm against *S. aureus*) for PLA films incorporating 3 wt% CNC-ZnO together with 20 wt% carvacrol; that system, however, relies on a volatile organic antimicrobial at a high loading, which raises concerns about progressive loss of activity during storage and about the mechanical penalty associated with such filler contents. In the present study, broad-spectrum activity is obtained from a non-volatile inorganic/biopolymer hybrid at a CS-ZnO loading of only 0.25 wt%, that is, at roughly an order of magnitude lower antimicrobial filler content, which is advantageous from both a cost and a regulatory perspective given the GRAS status of ZnO [12].

Table 3 places these results alongside neat PLA and representative commercial biodegradable films. The comparison requires one qualification. The tensile strengths quoted for commercial materials refer mainly to melt-extruded or oriented film, whereas the films studied here are unoriented and solvent cast, a route that gives lower absolute strength for any given polymer. The optimized composite is therefore not presented as stronger than commercial PLA film in absolute terms. What the comparison shows is that a solvent-cast film reaches a water vapour transmission rate roughly an order of magnitude below the other materials listed while also carrying antibacterial activity, which none of them provides.

Table 3. The optimized composite film compared with neat PLA and with representative commercial biodegradable packaging films.

Material	Tensile strength (MPa)	WVTR ($\text{g} \cdot \text{m}^{-2} \cdot 24\text{h}^{-1}$)	Antibacterial	Compostable
This work (PLA/5 wt% MNFC/0.25 wt% CS-ZnO)	31.4	3.15	Yes	Not tested
Neat PLA cast film	40–70	15–20	No	Yes
PBAT	22–28	60–120	No	Yes
PBS	30–40	300–500	No	Yes
Cellophane	60–110	300–1000	No	Yes

Values for commercial materials are typical ranges reported in the literature for solution-cast or extruded films and depend on grade, thickness, orientation and processing, so they are indicative rather than measured under identical conditions. Water vapour transmission rate in particular scales with film thickness, and the value for the present film refers to a thickness of approximately 100 μm . Compostability was not assessed experimentally in this work.

4. Conclusions

Multifunctional PLA composite films were prepared by solution casting using silane-modified nanofibrillated cellulose and chitosan-coated ZnO as dual fillers. Dissolving NFC in a $\text{ZnCl}_2/\text{AlCl}_3$ medium before KH-570 grafting converts cellulose from type I to type II, improving dispersibility in PLA and increasing the number of accessible sites for modification. The ZnO core of the CS-ZnO nanohybrid, prepared by co-precipitation and chitosan coating, has a crystallite size of 18.4 nm. FTIR shows that the recovered powder carries bands of both the polysaccharide and the oxide, confirming that chitosan is retained on the particle surface.

At 5 wt% MNFC with 0.25 wt% CS-ZnO, the films reach a tensile strength of 31.40 MPa, 113% above neat PLA, a crystallinity of 35.2%, a 4.1-fold increase, and a WVTR of 3.15 $\text{g}/\text{m}^2 \cdot 24 \text{ h}$, 79.3% lower than neat PLA, with inhibition zones of 18.3 mm against *E. coli* and 15.7 mm against *S. aureus*. Crystallization promoted by MNFC is the main route to the mechanical and barrier gains, while CS-ZnO supplies antibacterial activity and a compatibilizing interface. The antibacterial pathways themselves were not measured, and the account given above rests on the published literature rather than on data reported here. Zinc release, reactive oxygen species, surface charge and membrane damage all remain to be quantified, as do antibacterial durability under food contact, zinc migration, compostability under ISO 14855, and the behavior of the system under melt processing, where the reduced degradation onset observed by TGA would become significant.

Author contributions: The author contributed solely to the article.

Funding: This research received no external funding.

Data availability: All data supporting the findings of this study are available from the corresponding author upon reasonable request.

Conflict of interest: The authors declare no competing interests.

Declaration of competing interests: The authors declare no competing financial interests.

References

1. Shao L, Xi Y, Weng Y. Recent advances in PLA-based antibacterial food packaging and its applications. *Molecules*. 2022; 27(18): 5953. doi: 10.3390/molecules27185953
2. Rajendran DS, Venkataraman S, Jha SK, et al. A review on bio-based polymer polylactic acid potential on sustainable food packaging. *Food Science and Biotechnology*. 2024; 33(8): 1759–1788. doi: 10.1007/s10068-024-01543-x
3. Gao P, Masato D. The effects of nucleating agents and processing on the crystallization and mechanical properties of polylactic acid: A review. *Micromachines*. 2024; 15(6): 776. doi: 10.3390/mi15060776
4. Sharafi Zamir S, Fathi B, Ajji A, et al. Crystallinity and gas permeability of poly(lactic acid)/starch nanocrystal nanocomposite. *Polymers*. 2022; 14(14): 2802. doi: 10.3390/polym14142802
5. Hasoon K. T. N, Panicker UG. Beyond fossil plastics: next-generation PLA-based bio-packaging for industrial applications —advances, challenges, and data-driven insights. *RSC Advances*. 2026; 16(17): 15095–15118. doi: 10.1039/d5ra08379f
6. Ngwenya M, Gumede TP, Pérez Camargo RA, et al. Nanocellulose-reinforced poly(lactic acid) and poly(ϵ -caprolactone) bio-nanocomposites: A review and future outlook for poly(lactic acid)/poly(ϵ -caprolactone) blend systems. *Materials*. 2025; 18(22): 5172. doi: 10.3390/ma18225172
7. Yang M, Su J, Zheng Y, et al. Effect of different silane coupling agents on properties of waste corrugated paper fiber/polylactic acid composites. *Polymers*. 2023; 15(17): 3525. doi: 10.3390/polym15173525
8. Missoum K, Belgacem MN, Bras J. Nanofibrillated cellulose surface modification: A review. *Materials*. 2013; 6(5): 1745–1766. doi: 10.3390/ma6051745
9. Chu H, Chen Z, Chen Y, et al. Mechanical properties and crystallinity of specific PLA/cellulose composites by surface modification of nanofibrillated cellulose. *Polymers*. 2024; 16(17): 2474. doi: 10.3390/polym16172474
10. Guo M, Duan Y, Li Z, et al. Role of silane compatibilization on cellulose nanofiber reinforced poly(lactic acid) (PLA) composites with superior mechanical properties, thermal stability, and tunable degradation rates. *International Journal of Biological Macromolecules*. 2025; 297: 139836. doi: 10.1016/j.ijbiomac.2025.139836
11. Tong Y, Huang S, Meng X, et al. Aqueous-cellulose-solvent-derived changes in cellulose nanocrystal structure and reinforcing effects. *Polymers*. 2023; 15(14): 3030. doi: 10.3390/polym15143030
12. Youn SM, Choi SJ. Food additive zinc oxide nanoparticles: Dissolution, interaction, fate, cytotoxicity, and oral toxicity. *International Journal of Molecular Sciences*. 2022; 23(11): 6074. doi: 10.3390/ijms23116074
13. Sirelkhatim A, Mahmud S, Seeni A, et al. Review on zinc oxide nanoparticles: Antibacterial activity and toxicity mechanism. *Nano-Micro Letters*. 2015; 7(3): 219–242. doi: 10.1007/s40820-015-0040-x
14. El-Habib I, Maatouk H, Lemarchand A, et al. Antibacterial size effect of ZnO nanoparticles and their role as additives in emulsion waterborne paint. *Journal of Functional Biomaterials*. 2024; 15(7): 195. doi: 10.3390/jfb15070195
15. Wei Y, Wang J, Wu S, et al. Nanomaterial-based zinc ion interference therapy to combat bacterial infections. *Frontiers in Immunology*. 2022; 13: 899992. doi: 10.3389/fimmu.2022.899992
16. Dadashi P, Bonsale R, Babaei A. Chitosan/ZnO nanohybrid as an efficacious compatibilizer for PLA/PBS blend suitable candidate for biodegradable packaging applications. *Scientific Reports*. 2025; 15(1): 41661. doi: 10.1038/s41598-025-25596-y
17. Babaei-Ghazvini A, Acharya B, Korber DR. Antimicrobial biodegradable food packaging based on chitosan and metal/metal-oxide bio-nanocomposites: A review. *Polymers*. 2021; 13(16): 2790. doi: 10.3390/polym13162790
18. Zheng H, Chen L, Liu T, et al. Poly-(lactic acid) composite films comprising carvacrol and cellulose nanocrystal-zinc oxide with synergistic antibacterial effects. *International Journal of Biological Macromolecules*. 2024; 266(Pt 1): 130937. doi: 10.1016/j.ijbiomac.2024.130937

19. Ramike MP, Ndungu PG, Mamo MA. Exploration of the different dimensions of wurtzite ZnO structure nanomaterials as gas sensors at room temperature. *Nanomaterials*. 2023; 13(20): 2810. doi: 10.3390/nano13202810
20. Radmehr M, Poursattar Marjani A, Akhavan A. Synthesis and characterization of antibacterial CMC/AAc/ZnO nanocomposite superabsorbent using gamma radiation. *Scientific Reports*. 2025; 15(1): 9345. doi: 10.1038/s41598-025-93884-8
21. Reddy TRK, Jayaramudu T, Varaprasad K, et al. A review on nanocellulose in food packaging: A paradigm shift for enhanced mechanical strength and barrier performance. *International Journal of Biological Macromolecules*. 2025; 322(Pt 1): 146672. doi: 10.1016/j.ijbiomac.2025.146672