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Enhancement of Physicochemical, Thermal, and Antibacterial Properties of Chitosan/PVA Films by Eggshell-Derived CaO nanoparticles

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Abstract

Calcium oxide (CaO) nanoparticles were prepared using domestic eggshell waste through thermal calcination and incorporated into chitosan/polyvinyl alcohol (CS/PVA) composite to improve their physicochemical and antibacterial properties. CS, CS/PVA, and CS/PVA/CaO formulations were synthesized and evaluated using viscosity measurements, FTIR, XRD, SEM, and antibacterial activity against *Escherichia coli*. FTIR and XRD indicated the presence of crystalline CaO with traces of residual carbonate, while SEM analysis indicated dramatic morphological improvements, especially enhanced porosity and surface roughness upon CaO addition. Viscosity determinations indicated concentration-dependent increase, with CS/PVA and CS/PVA/CaO solutions having lower viscosities than neat chitosan, suggesting enhanced chain mobility and processability. TGA analysis showed enhanced thermal stability in the CS/PVA/CaO films compared with CS and CS/PVA films, demonstrating the reinforcing effect of CaO nanoparticles in the polymer matrix. Antibacterial analysis showed that the CS/PVA sample had the largest inhibition zone compared to CS and CS/PVA/CaO, indicating a synergistic effect between CS and PVA, while the introduction of CaO reduced antibacterial activity slightly, likely because of nanoparticle aggregation. In all, this paper points to a green process to transform biowaste into functional nanomaterials and secures a structure–property–function relationship in CS-based antimicrobial films, supporting their potential application in biomedical, environmental, and packaging fields.

Keywords: CaO nanoparticles, CS/PVA/CaO blend, physicochemical enhancement, antibacterial analysis

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1. Introduction

Chitosan (CS) is a natural, linear, polycationic polymer made by partially removing acetyl groups from chitin. Chitin is the main structural component of the exoskeletons of crustaceans. Chemically, chitosan is a linear heteropolysaccharide that consists of β-1,4-linked D-glucosamine and N-acetyl-D-glucosamine units [1]. Owing to its biocompatibility, biodegradability, and notable antibacterial and antifungal properties, chitosan has gained widespread attention for applications in biomedical, environmental, and industrial fields [2, 3].

Despite its many advantages, chitosan also exhibits certain drawbacks, including brittleness, poor solubility at neutral and basic pH, and low mechanical strength. These limitations can be addressed by blending or grafting chitosan with natural or synthetic polymers such as cellulose, alginate, polyethylene glycol (PEG), or polyvinyl alcohol (PVA) [4]. Such modifications enhance its mechanical strength, flexibility, and water solubility, thereby improving its performance in food packaging, water treatment, and biomedical applications [5].

PVA is a water-soluble synthetic polymer that is considered safe, non-toxic, and biocompatible. This makes it highly suitable for diverse applications [6]. Unlike many synthetic polymers that require organic solvents for processing, PVA dissolves readily in water due to the presence of hydroxyl (-OH) groups, which facilitate hydrogen bonding with water molecules [7]. Blending PVA with chitosan improves the hydrophilicity and thermal durability, thereby expanding its applicability in sectors such as drug delivery and wound dressing [8]. The strong intermolecular hydrogen bonding between PVA and chitosan enhances the composite's structural integrity, resulting in a more amorphous and flexible material [9].

Incorporating nanoparticles into polymer matrices further enhances the material's structural, mechanical, and functional properties, including chemical stability,

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electrical conductivity, optical behavior, and swelling capacity [10]. Uniform dispersion of nanoparticles within the polymer matrix is essential for reinforcing these characteristics, as it affects the material microstructure and molecular interactions. Metal oxide nanoparticles such as titanium dioxide (TiO_2), zinc oxide (ZnO), and calcium oxide (CaO) have shown strong antibacterial effectiveness. They can generate reactive oxygen species (ROS) and disrupt microbial cell membranes. [11].

Calcium oxide nanoparticles (CaO NPs), in particular, exhibit potent antibacterial and antifungal properties by generating reactive oxygen species (ROS) and increasing environmental alkalinity, thereby compromising bacterial cell membranes and causing cell death [12]. Moreover, CaO NPs can be synthesized from natural waste materials such as eggshells, making the process cost-effective and environmentally sustainable [13]. This eco-friendly approach not only reduces production costs but also supports waste valorization and circular economy initiatives [14].

Sutharsan et al. demonstrated that chitosan/polyvinyl alcohol (CS/PVA)–based nanocomposite films incorporated with g-C_3N_4 exhibit enhanced thermal stability, photocatalytic activity, and antimicrobial performance while maintaining smooth film morphology [15]. Their findings emphasize that the incorporation of inorganic nanofillers into CS/PVA matrices effectively improves structure–property relationship without compromising film integrity. These results highlight the potential of CS/PVA-based nanocomposites as sustainable antimicrobial materials and support further investigation of alternative green nanofillers, such as eggshell-derived CaO nanoparticles.

Lishchynskyi et al. reported the development of a temperature-responsive POEGMA (poly(di(ethylene glycol) methyl ether methacrylate) polymeric brush, which, when integrated with $CaCO_3$ nanoparticles, functioned as a biologically active substrate with promising applications in tissue engineering [16].

The physical and chemical characteristics of chitosan-based composites, such as viscosity, morphology, and crystallinity, are crucial for determining their suitability in practical applications [17]. Viscosity, a key rheological parameter, affects the processability and film-forming ability of the material [18]. Blending chitosan with PVA alters its viscosity profile, which may be further influenced by the incorporation of CaO NPs due to modified polymer–nanoparticle interactions [19,20]. Understanding these variations is essential for optimizing processing parameters and ensuring consistency in performance [21]. Ormazábal et al. reported that eggshell-derived CaO nanoparticles can be effectively utilized as antimicrobial fillers in polymer matrices, demonstrating a significant *E. coli* reduction and improved structural properties when well dispersed [22]. Their findings highlight that nanoparticle surface characteristics strongly influence antimicrobial efficiency and composite performance, suggesting that incorporating biowaste-derived CaO into biodegradable polymer matrices such as chitosan/PVA could further enhance antibacterial functionality and sustainability.

Morphological features, particularly surface texture and microstructure, significantly influence the functional properties of composites. Techniques such as scanning electron microscopy (SEM) provide valuable insights into component dispersion, homogeneity, and porosity [23]. The inclusion of PVA and CaO NPs can modify these morphological characteristics, thereby affecting mechanical strength and barrier properties of the composite [24].

This study aims to investigate the viscosity, surface morphology (SEM), and antibacterial activity of pure chitosan, chitosan–PVA, and chitosan–PVA–CaO composites. By examining these properties, we seek to elucidate the synergistic effects of PVA and CaO nanoparticles on the chitosan matrix, with the ultimate goal of developing enhanced biomaterials for a range of biomedical and industrial applications.

2. Materials and Methods

2.1 Materials

The polymers used in this study were polyvinyl alcohol (PVA), with a molecular weight of 85,500 $g \cdot mol^{-1}$ and a degree of hydrolysis of 89.5% and chitosan (CS) with a degree of deacetylation of 68.5% purchased from Sigma-Aldrich. Glacial acetic acid from Merck was used to prepare CS solutions. Domestic eggshells were used to synthesize calcium oxide nanoparticles.

2.2 Synthesis of CaO NPs

The experimental procedure followed for the preparation of eggshell-derived CaO is schematically shown in Figure 1. Chicken eggshells were collected from kitchen waste and washed with deionized (DI) water to remove unwanted residues. It was heated to 100 °C and ground to fine powder in a mixer grinder. This eggshell powder obtained was calcined at 900 °C for 2 h. It was cooled to around 100 °C, and the resulting CaO powder was crushed using a mortar and pestle to fine powder with a nanoscale particle size, as shown in Figure 1 [25].

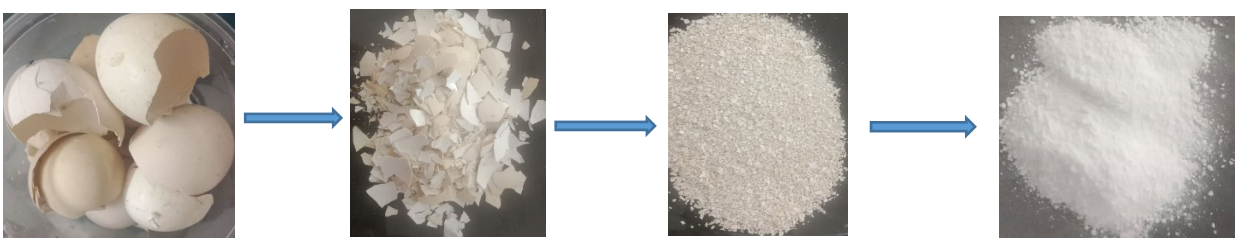


Figure 1. Preparation of eggshell derived CaO nanoparticles by calcination.

2.3 Preparation of CS, CS/PVA and CS/PVA/CaO solution mixture

A 1% (w/v) CS solution was prepared by dissolving chitosan powder in a 1% (v/v) acetic acid solution under continuous stirring at room temperature until a clear and homogeneous solution was obtained [26].

For the preparation of the CS/PVA solution, polyvinyl alcohol (PVA) was first dissolved in distilled water by heating to approximately 80 °C with constant stirring until completely dissolved. The chitosan solution was then added to the PVA solution in a 1:1 (v/v) ratio, and the mixture was stirred at room temperature until a uniform blend was achieved [27].

To prepare the CS/PVA/CaO composite solution, 0.5 g of calcium oxide (CaO) powder was gradually introduced into the CS/PVA mixture under vigorous stirring to ensure uniform dispersion. The resulting suspension was then subjected to ultrasonication until a stable and homogeneously mixed formulation was obtained [28].

2.4 Viscosity measurement

Stock solutions of CS, CS/PVA and CS/PVA/CaO were prepared. From these stock solutions, five concentrations (0.1%, 0.2%, 0.3%, 0.4%, and 0.5% w/v) were prepared by dilution with distilled water under continuous stirring at room temperature to ensure homogeneity. For each formulation, the required volume of 1% stock solution was mixed with distilled water to achieve the target concentration, following the dilution formula:

$$C_1V_1=C_2V_2$$

Where C_1 and V_1 are the concentration and volume of the stock solution, and C_2 and V_2 are the desired concentration and final volume, respectively. Each diluted solution was stirred gently for 30 minutes.

The viscosity of each solution was measured using an Ubbelohde capillary viscometer. The viscometer was thoroughly cleaned, rinsed with distilled water, and dried before use. Approximately 15 mL of each test solution was introduced into the viscometer. The efflux time, defined as the time required for the solution to flow between the two marked levels, was recorded using a digital stopwatch. Each sample was measured in duplicate, and the mean efflux time was used for viscosity calculations [29].

2.5 Antibacterial activity

Antibacterial efficacy of chitosan, chitosan/PVA, and chitosan/PVA/CaO solutions was tested against *Escherichia coli (E. coli)* by agar well diffusion method [30]. The nutrient agar media were prepared and sterilized and then transferred to sterile Petri dishes and left to set. *E. coli* was cultured fresh in nutrient broth and diluted to standardized turbidity (equivalent to 0.5 McFarland standard). The bacterial suspension was evenly spread on the surface of the agar plates using a sterile cotton swab in order to get a uniform lawn growth. Wells of diameter 6 mm were then punctured into the agar, and 100 µL of each test solution (Chitosan, Chitosan/PVA, and Chitosan/PVA/CaO) was aseptically filled in separate wells. A control well containing sterile distilled water was also included in order to verify the results.

The plates were incubated at 37 °C for 24 hours, and afterward the antibacterial activity was determined by the measurement of the zone of inhibition around each well. The procedure was carried out in triplicate to ensure reproducibility, and the mean zone of inhibition for every sample was determined. The relative antibacterial activity of the samples was determined from the diameter of the inhibition zones, larger zones denoting greater antibacterial activity. The procedure enabled a qualitative and semi-quantitative evaluation of the bactericidal activity of the various chitosan-based formulations against *E. coli*.

2.6 FE-SEM Analysis

Field Emission Scanning Electron Microscopy (FE-SEM) was employed to investigate the surface morphology of the prepared chitosan, chitosan/PVA, and chitosan/PVA/CaO films. FE-SEM imaging was carried out on a FE-SEM model JEOL JSM-7610F under high-vacuum condition at an accelerating voltage of 5 kV. Images were taken at various magnifications in order to evaluate surface features like homogeneity, porosity, smoothness and the distribution of embedded particles.

2.7 Thermo gravimetric Analysis

Thermo gravimetric analysis (TGA) was used to assess the thermal stability and decomposition pattern of prepared samples. The experiment was conducted on a TGA analyzer (Model: SETLINE, Manufacturer: LCGC) in a nitrogen environment to avoid oxidative degradation. About 20 mg of each dried sample was loaded in a platinum crucible and heated from room temperature to 800 °C at a constant heating rate of 10 °C/min. The weight loss and its respective temperature were measured to evaluate the thermal decomposition profile of the materials.

2.8 Water vapor permeability rate of films

The water vapor permeability rate of polymeric films was determined using the gravimetric cup method in accordance with ASTM E96/E96M. In this method, the test film is sealed over the mouth of a permeation cup that contains either a desiccant or distilled water, depending on whether the dry-cup or wet-cup procedure is employed. The assembly is placed in a controlled environment, and the increase or decrease in the cup's mass due to water vapor transfer through the film is recorded at regular time intervals until steady-state permeation is achieved.

3. Results and Discussion

3.1 Characterisation of CaO nanoparticles

In the FTIR spectrum of the synthesized calcium oxide (CaO) nanoparticles, several characteristic absorption bands were identified, confirming the presence of specific functional groups associated with both the target compound and residual precursors. The absorption

band observed at 710 cm^{-1} is attributed to the Ca–O bond vibration, indicating the successful formation of calcium oxide. A peak at 869.90 cm^{-1} corresponds to the C–O vibrational mode of calcium carbonate ($CaCO_3$), suggesting the presence of residual carbonate species likely resulting from incomplete thermal decomposition of the precursor material. Additionally, the band at 1514 cm^{-1} is associated with the asymmetric stretching vibrations of carbonate ions (CO_3^{2-}), further supporting the presence of minor $CaCO_3$ content. A broad absorption band at 3639.68 cm^{-1} was also detected, corresponding to the O–H stretching vibration of water molecules coordinated to calcium, which is indicative of adsorbed moisture on the nanoparticle surface. These findings confirm the formation of CaO while also highlighting the partial retention of carbonate species and surface-bound water, which are common in CaO materials synthesized from natural sources such as eggshells.

X-ray diffraction (XRD) analysis further validated the crystalline nature of the calcined eggshell powder. The XRD pattern showed sharp and intense diffraction peaks within the 2θ range of 30 ° – 90 °, characteristic of well-crystallized CaO. The average crystallite size was estimated using the Scherrer equation, confirming nanoscale dimensions. Together, these analyses demonstrate that the synthesized CaO nanoparticles exhibit a predominantly crystalline structure with minor residual carbonate content and surface-bound moisture — typical traits for CaO derived from bio-waste materials.

3.1.1 JCPDS data

The crystalline phases in the sample were identified by comparing the experimentally obtained XRD pattern with standard JCPDS data. The XRD pattern exhibits distinct diffraction peaks that closely match the standard diffraction data of calcium oxide (CaO), confirming that CaO is indeed formed in the sample. The strong diffraction peaks observed at about 2θ = 32.2°, 37.4°, 53.9°, 64.2°, and 67.4° correspond to the reflections from the (111), (200), (220), (311), and (222) crystallographic planes, respectively. These peaks are reasonably matched to the JCPDS PDF No. 37-1497: CaO with a cubic crystal system and an FCC lattice. The close match between peak position and relative intensities with JCPDS reference data provides evidence for the crystalline nature and phase purity of CaO. Besides, no additional diffraction peaks due to either $CaCO_3$ or $Ca(OH)_2$ were found in the XRD spectrum, indicating that calcination was effective and that the eggshell-derived calcium precursor had successfully transformed into CaO.

3.1.2 TEM and AFM analysis of CaO nanoparticles

The TEM analysis gives a very clear and high-magnification image of individual nano-calcium oxide particles from eggshell powder, which can distinctly attest to their morphology and size (Fig. 4a). The micrographs show particles with a spherical, hemispherical, or quasi-cubic shape with very distinct edges. The measurements from the scale bar of the micrograph will show that these particles have nano-scale dimensions, with an average size measured between 10 nm and 50 nm. The particles are very small in dimension, which is very important since they have a high surface area to volume ratio; this is highly advantageous especially in heterogeneous catalysis and absorption. The distinct lattice fringes in HR-TEM analysis will attest to a very high level of crystallinity in the calcium oxide samples with a face-centered cubic structure. In AFM imaging, the focus is on the three-dimensional surface morphology and texture of the nano-CaO when used in film form or a dispersed layer (Fig. 4b). Color scale in this image clearly indicates granular/irregular surface morphology, establishing a two-dimensional array of these self-assembled nanoparticles. More sensitively, AFM provides information concerning surface roughness on a scale measured in nanometers in terms of root mean square (RMS) roughness or average roughness (Ra).

3.2 Viscosity measurement

The viscosities of chitosan, chitosan/PVA, and chitosan/PVA/CaO solutions at concentrations of 0.1%, 0.2%, 0.3%, 0.4%, and 0.5% were measured using an Ostwald viscometer. The measured values are presented in Table 1.

The viscosities of all three formulations increase as concentration increases. This is consistent with the overall behavior of polymer solutions, in which increased

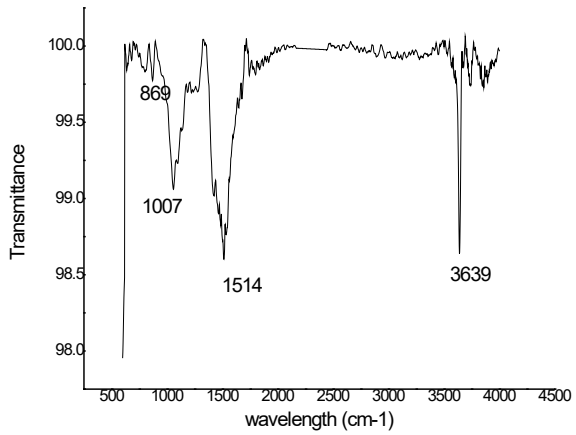


Figure 2. The FTIR spectrum of CaO nanoparticles derived from eggshell powder.

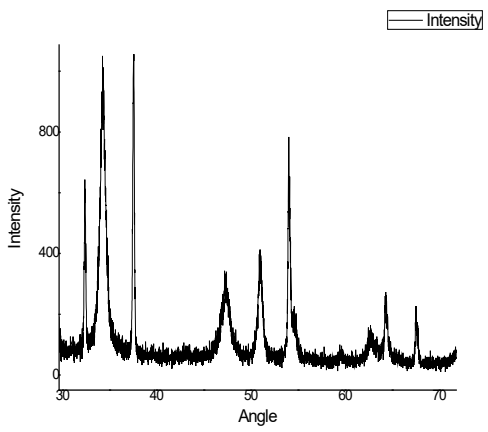


Figure 3. The XRD spectrum of CaO nanoparticles.

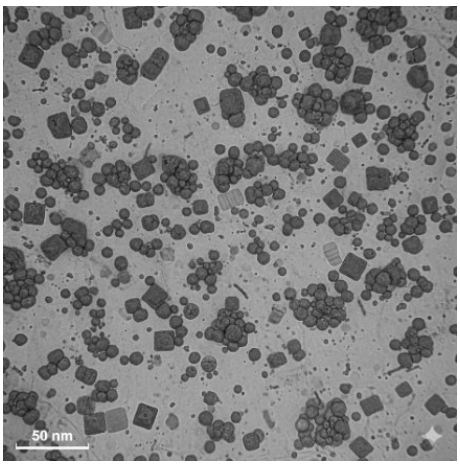


Figure 4a. The TEM image of CaO nanoparticles

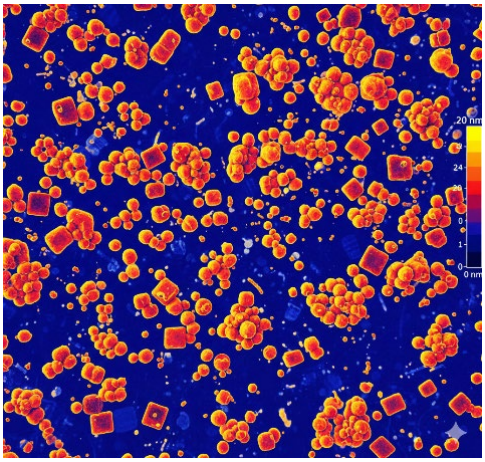


Figure 4b. The AFM images of CaO nanoparticles

Table 1. Viscosity of chitosan, chitosan/PVA, and chitosan/PVA/CaO.

Concentration (%)	Viscosity of Chitosan (Poise)	Viscosity of chitosan/PVA (Poise)	Viscosity of blend (Poise)
0.1	0.0391	0.0128	0.00981
0.2	0.0659	0.0153	0.0107
0.3	0.0867	0.0172	0.0115
0.4	0.1218	0.0189	0.0127
0.5	0.1591	0.0215	0.0137

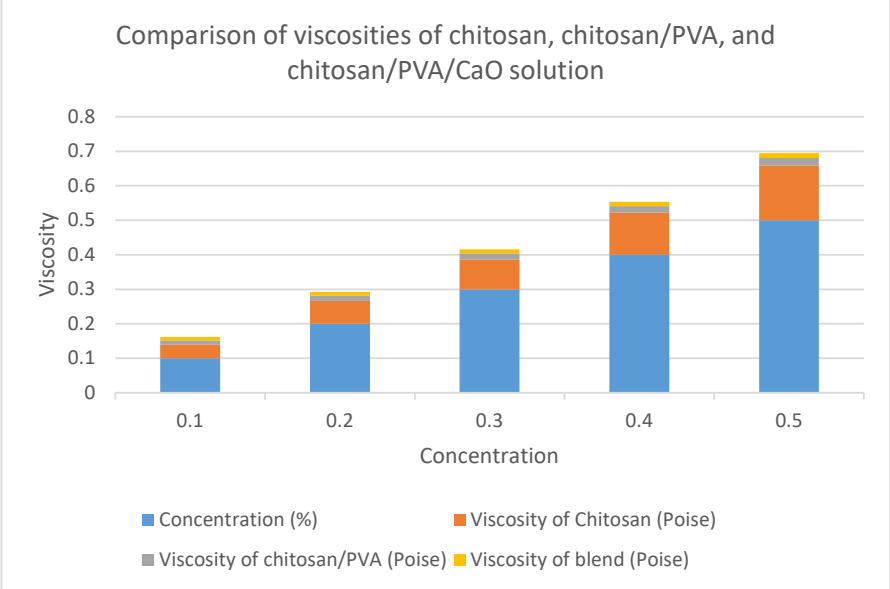


Figure 5. Comparison of viscosities of chitosan, chitosan/PVA, and chitosan/PVA/CaO solution.

concentrations lead to greater molecular entanglements and interactions and, therefore, greater resistance to flow.

Among the three formulations, pure chitosan solutions have the highest viscosity at all concentrations. This is likely because of the high molecular weight of chitosan and the extensive intra- and intermolecular hydrogen bonding between the chains of chitosan, leading to a more viscous and ordered solution. By comparison, the CS/PVA blend solutions have much lower viscosities than pure chitosan. Combining PVA with chitosan probably interferes with some of the chitosan-chitosan interactions and decreases the overall viscosity. This reduction is due to the more flexible and linear nature of PVA, which reduces the stiffness of chitosan and enhances chain mobility in the solution.

The CS/PVA/CaO solutions exhibited the lowest viscosities among the three formulations. The introduction of calcium oxide nanoparticles likely disrupted the interactions between the polymer chains and further

reduced the viscosity, possibly by increasing the distance between the polymer chains or interfering with hydrogen bonding. The nanoparticles may also promote more compact polymer chain conformations, resulting in a reduction in hydrodynamic volume and, consequently, lower viscosity. In general, the findings shows that both CaO incorporation and PVA blending result in reduced viscosity compared to solutions of pure chitosan. These rheological changes have important implications for processing and application. Reduced-viscosity products might be better suited for spraying, electrospinning, or film casting, depending on application requirements.

3.3 Antibacterial analysis

The antibacterial activity of the developed films was assessed against *Escherichia coli (E. coli)* using the agar well diffusion method. A comparative analysis was performed among chitosan (CS), chitosan/polyvinyl alcohol (CS/PVA), and chitosan/polyvinyl alcohol/calcium oxide (CS/PVA/CaO) composite films. Nalidixic acid, used as the standard antibiotic control, exhibited the largest zone of inhibition at 2.0 cm, confirming the sensitivity of *E. coli* to antimicrobial agents. The CS film alone showed a moderate inhibition zone of 1.2 cm, attributed to the intrinsic antibacterial properties of chitosan, which is known to disrupt bacterial cell membranes. Upon blending with PVA, the CS/PVA film demonstrated an increased zone of inhibition of 1.6 cm. This suggests that the incorporation of PVA improved the film's antibacterial performance, possibly by promoting better film formation and facilitating the sustained release of active components. The addition of CaO, synthesized from eggshell powder (ESP), to the CS/PVA matrix resulted in a slight reduction in antibacterial activity, with a zone of inhibition of 1.0 cm. Although CaO alone displayed a limited antibacterial effect (0.7 cm), its incorporation into the polymeric matrix did not enhance the activity beyond that of CS or CS/PVA alone. This suggests that while CaO contributes to the antimicrobial profile, its interaction with the CS/PVA matrix may influence the overall effectiveness, potentially due to factors such as reduced diffusion or particle aggregation. Overall, the CS/PVA film demonstrated the highest antibacterial activity among the composites, indicating a more effective combination for antimicrobial applications compared to the CaO-loaded variants.

Table 2. The zone of inhibition of different components against *E. coli*.

Bacteria -*E Coli*	Zone of inhibition (cm)
Nalidixic acid	2
Chitosan	1.2
Chitosan + PVA	1.6
CaO (ESP)	0.7
Chitosan + PVA+ CaO (ESP)	1

3.4 Preparation and Characterization of Chitosan, Chitosan/PVA, and Chitosan/PVA/CaO films

Chitosan and PVA/chitosan films, were obtained by solution casting. Initially, chitosan was dissolved in a 1% (v/v) acetic acid solution and stirred until a clear solution was obtained. The solution was then poured over a clean, flat surface and drying was performed under controlled conditions. This process resulted in the formation of chitosan films. For the preparation of PVA/chitosan/CaO films, PVA was first dissolved in distilled water at 90 °C. Chitosan solution was then added to it, and stirring was continued until a uniform mixture was formed. Finally, CaO nanofillers were added, followed by vigorous stirring and ultrasonic treatment. The resulting solution was then dried to form uniform and flexible PVA/chitosan/CaO composite films.

PVA and chitosan are generally considered to be miscible or highly compatible polymers due to strong intermolecular hydrogen bonding between the hydroxyl groups of PVA and the hydroxyl and amine groups of chitosan, which promotes the formation of a homogeneous polymer network without clear phase separation. When a nanofiller is introduced into this miscible PVA/chitosan blend, it does not reside exclusively in either the PVA or chitosan phase; instead, it preferentially localizes at the polymer–polymer interface, where it can interact simultaneously with functional groups from both polymers. In the case of polar inorganic fillers such as CaO, strong interactions with the –OH groups of PVA and the –OH/–NH_2 groups of chitosan are favored, allowing the filler to act as an interfacial reinforcing and functional agent, thereby enhancing the structural stability and overall performance of the composite system.

Temperature plays an important role in the solubilization and homogeneous preparation of the chitosan/PVA/CaO blend, mainly because it controls the dissolution of the polymers, along with viscosity and interfacial interactions. For instance, moderate heating, such as 40 °C, enhances the dissolution of chitosan in dilute acetic acid, due to increased chain mobility and protonation of amino groups, while high temperatures up to 70 °C disrupt the hydrogen bonding among the PVA molecules, leading to their complete dissolution. However, if the temperature is too high, it may potentially allow hydration of CaO or partial decomposition of chitosan to take place prematurely, which would reduce the stability and uniformity of the blend. Therefore, controlled temperature conditions are required to achieve effective solubilization and uniform distribution of fillers for the preparation of a stable chitosan/PVA/CaO blend suitable for film formation.

The solubilized chitosan/PVA/CaO polymer blend can affect the growth of plants in a dual manner by acting directly on the plants or indirectly by reacting with the soil and water.

3.4.1 Water vapor permeability rate of films

The water vapor permeability rate (WVPR) is calculated from the slope of the linear portion of the mass change versus time plot divided by the exposed film area. The water vapor permeability (WVP) is then obtained by multiplying the WVPR by the film thickness and dividing by the water vapor pressure difference across the film.

Figure 6. Antibacterial analysis of CaO, CS, CS/PVA, and CS/PVA/CaO.

Lower WVP values indicate improved barrier properties, which in chitosan/PVA-based films are influenced by polymer miscibility, hydrogen bonding, crystallinity, and the dispersion of fillers such as CaO that can increase tortuosity and reduce moisture diffusion.

The water contact angle measures how a droplet of water interacts with a solid surface. It is used to assess the wettability of a surface and to determine whether it is hydrophilic or hydrophobic. When a small droplet of distilled water lands on a solid surface, its shape depends on the surface energy of the material. A low contact angle, less than 90°, shows that water spreads easily on the surface, indicating hydrophilic behavior. In contrast, a high contact angle, more than 90°, means poor wetting and hydrophobic behavior. In polymer films like chitosan/PVA-based materials, the water contact angle is greatly affected by surface chemistry, roughness, and the presence of hydrophilic functional groups (–OH and –NH_2). Adding fillers like CaO can change surface energy and roughness, leading to a lower contact angle and better wettability. This property is especially important for applications such as water purification and filtration, as lower contact angles allow for better water penetration and interaction with the active antibacterial surface.

Degradation analysis of films was carried out to assess the stability and degradation behavior of polymer composites under environmental or controlled conditions. Chitosan degradation occurs mainly by microbial and enzymatic action, while PVA undergoes hydrolytic and microbial degradation at a slower rate; combining the two in a blend enables a controlled degradation profile. The presence of inorganic fillers like CaO influences degradation through the alteration of the pH and moisture uptake, generally accelerating the initial degradation by increasing hydrophilicity and microstructural disruption of the polymer matrix. Consequently, these composites reduce long-term plastic accumulation, lower the generation of microplastics, and ensure low ecological toxicity.

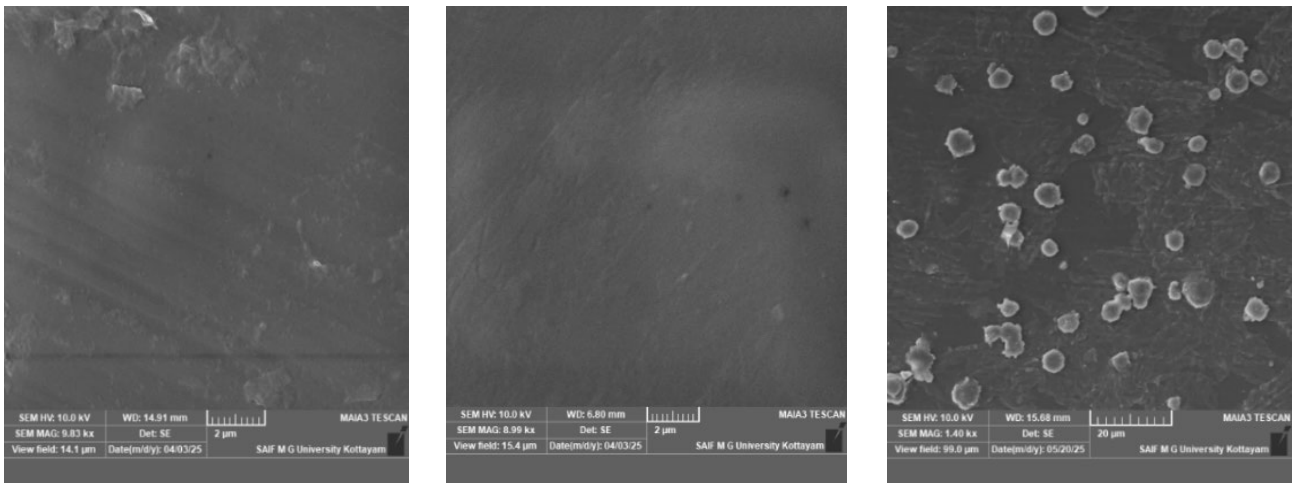
Water uptake and swelling properties of both the solutions and films prepared from the chitosan/PVA/CaO blend are primarily governed by the hydrophilic nature of chitosan and PVA and the interaction of CaO within the polymer matrix. In the solid film stage, the controlled incorporation of CaO affects swelling due to the fact that this inorganic filler may improve water uptake by enhancing porosity or reduce excessive swelling due to ionic interactions with chitosan chains. Balanced swelling improves flexibility, permeability, and functional performance of the film, whereas excessive swelling can reduce mechanical stability.

The water solubility of the chitosan/PVA/CaO blend solution and the resulting film is mainly related to the intrinsic solubility of the polymers and their intermolecular interactions. PVA naturally has excellent water solubility due to the high density of its hydroxyl groups, while chitosan is insoluble in neutral water but soluble in dilute acidic media because of the protonation of its amino groups. In the blended system, this results in hydrogen bonding between chitosan and PVA, which reduces the number of free hydrophilic sites and thereby limits complete dissolution in water, while still allowing partial solubility and swelling. Water solubility of the film is further reduced by the addition of CaO, which, besides acting as an inorganic crosslinking agent, also increases structural rigidity through ionic interactions with chitosan chains.

3.5 SEM analysis

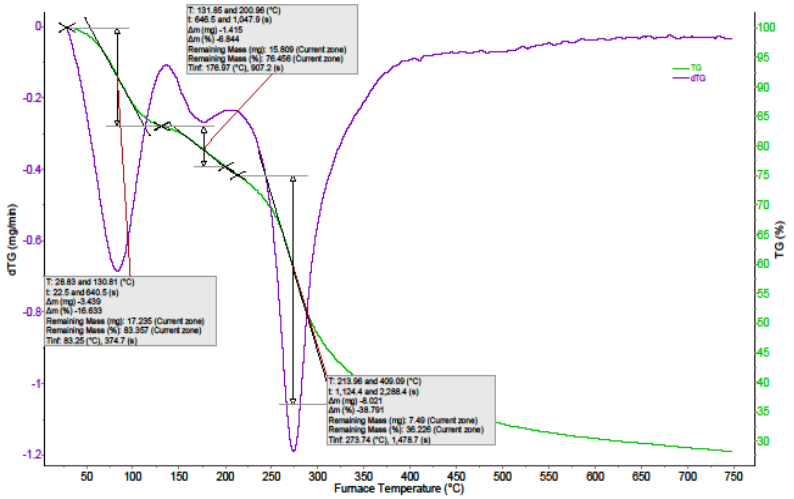
The SEM analysis of the chitosan, chitosan/PVA and chitosan/PVA/CaO films reveals marked differences in the morphology, showing the influence of blending and the addition of nanofillers on film structure. The homopolymer chitosan film possesses a surface that is rough, irregular, and compact with minimal porosity. The surface has aggregated areas and no uniformity of fiber or phase distribution, which explains the inherent brittleness and poor film-forming character of chitosan when applied as a pure material. These features are common because of the high viscosity and intermolecular hydrogen bonding of chitosan, which inhibits it from presenting smooth or continuous structures. The absence of pores and compactness of the surface can restrict its functional characteristics such as flexibility, permeability, and surface area, which play an important role when used in biomedical or filtration applications.

With the addition of PVA into the chitosan matrix, surface morphology is greatly enhanced. The chitosan/PVA

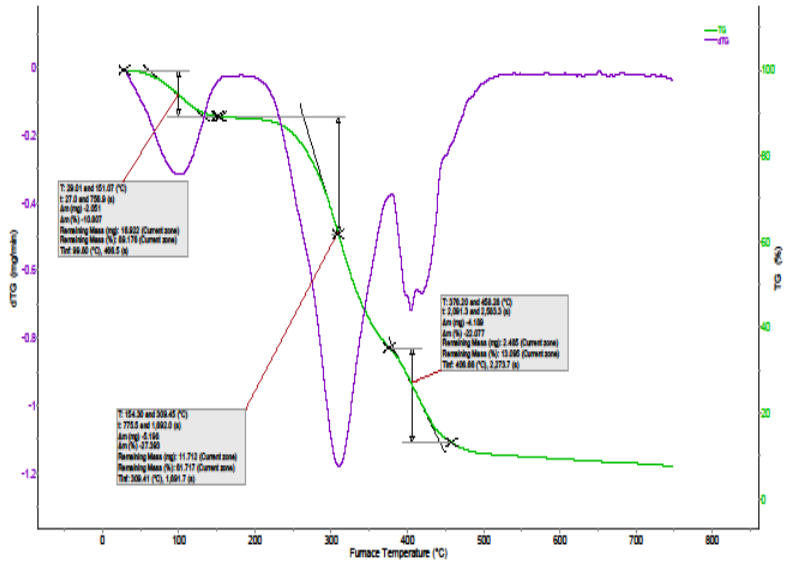


Chitosan Chitosan/PVA Chitosan/PVA/CaO

Figure 7. The SEM images of chitosan, chitosan/PVA, and Chitosan/PVA/CaO.



Chitosan



Chitosan/PVA

Figure 8. The TGA curves of CS, CS/PVA, and CS/PVA/CaO films.

blend film exhibits a smoother, more uniform texture with enhanced phase distribution, and this can be explained by the plasticizing effect and hydrophilic nature of PVA. The film surface is more flexible and contiguous with enhanced porosity and reduced surface defects. Further alteration with CaO nanoparticles in the chitosan/PVA/CaO film produces a significant change in morphology. The SEM micrograph of this composite film shows a rougher and more porous surface with particulate features dispersed likely resulting from embedded CaO. These particles seem to be evenly distributed, forming micro-roughness and increasing the surface area. Such increased porosity and surface heterogeneity may increase antibacterial activity and interaction with aqueous media. In summary, the morphological progression from chitosan to chitosan/PVA/CaO exhibits enhanced structural characteristics, and the resulting composite film provides a favorable combination of uniformity, porosity, and nanostructural incorporation for sophisticated functional uses.

3.6 Thermogravimetric analysis

The thermal stability of chitosan (CS), chitosan/polyvinyl alcohol (CS/PVA), and chitosan/polyvinyl alcohol/calcium oxide (CS/PVA/CaO) films was determined using thermogravimetric analysis (TGA). The TGA and the derivative TGA (DTG) curves for the three samples are shown in Figure 8. All the samples shows multiple clear phases of weight loss due to moisture evaporation, polymer degradation, and degradation of the polymer matrix, and the remaining inorganic content.

The CS film displayed three major decomposition stages. The initial weight loss (16.63%) occurred from 28.8 °C to 130.8 °C due to the evaporation of bound water. This was followed by a minor degradation phase (6.84%) from 131.9 °C to 200.9 °C, attributed to the breakdown of low molecular weight fractions. The primary thermal degradation (38.79%) occurred between 213.9 °C and 409.1 °C, indicating the decomposition of the polymer backbone, resulting in a residual mass of 36.23% at the end of the heating cycle.

The thermal profile for the CS/PVA film was slightly better. The initial stage of degradation (10.81%) occurred from 29.0 °C to 151.1 °C. This was succeeded by a significant weight loss of 27.39% between 154.3 °C and 309.5 °C, representing polymer degradation. There was another stage of decomposition (22.08%) between 376.2 °C and 458.3 °C, indicating more thermally stable interactions between CS and PVA. The residual mass was decreased to 13.10%, which is a sign of higher thermal decomposition than for pure chitosan.

The addition of CaO to the CS/PVA matrix drastically changed the thermal profile. The CS/PVA/CaO film showed initial degradation (12.52%) between 31.7 °C and 162.3 °C. A significant decomposition phase (54.87%) was observed from 214.2 °C to 388.1 °C. A third degradation step (3.67%) was also seen at a higher temperature range of 674.7 °C to 746.9 °C, which is due to decomposition of remaining carbonaceous materials or interactions with CaO. The final residual mass reached a minimum of 9.32%, reflecting improved decomposition efficiency, which may be a result of catalytic action of CaO nanoparticles.

These findings clearly indicate that the addition of PVA enhances the thermal stability of chitosan films, and additional CaO nanoparticles add to this stability by moving the degradation towards higher temperatures and facilitating further degradation of the polymer matrix. The CS/PVA/CaO film thus exhibits superior thermal resistance, making it suitable for applications requiring high thermal stability.

4. Conclusion

Calcium oxide (CaO) nanoparticles were successfully synthesized from waste eggshells via a simple thermal decomposition method and were subsequently incroporated into chitosan/polyvinyl alcohol (CS/PVA) composite films. Comprehensive structural and morphological characterizations, including FTIR and SEM analyses, confirmed the successful formation of CaO and its homogenous dispersion within the polymeric blend.

Viscosity studies revealed that the addition of PVA and CaO significantly reduced the viscosity of chitosan solutions, indicating enhanced polymer chain flexibility and improved processability. This reduction in viscosity suggests that these modified systems may be more suitable for applications involving film casting, electrospinning, or coating technologies, where lower viscosity is advantageous. Thermogravimetric analysis (TGA) also proved that the addition of CaO nanoparticles in the CS/PVA matrix improved the thermal stability of the films. The CS/PVA/CaO films showed a better decomposition temperature and higher thermal resistance than pure CS and CS/PVA films, verifying the reinforcing capability of CaO on the thermal behavior of the biopolymer composites.

Antibacterial assays against *Escherichia coli* revealed that the CS/PVA film produced the largest inhibition zone, highlighting a favorable synergism between chitosan's cationic sites and PVA's hydrophilicity. Although adding CaO did not further boost antibacterial efficacy, it created a rougher, more porous surface that could be advantageous for other functions (e.g., adsorption, catalytic supports, or tissue-engineering scaffolds).

Overall, this study presents a sustainable approach for converting eggshell waste into functional CaO nanofillers and establishes clear structure–property relationships across pure CS, CS/PVA, and CS/PVA/CaO systems. Future research should focus on optimizing CaO loading, evaluating antimicrobial activity against a broader spectrum of pathogens, and investigating the long-term mechanical stability and reusability of the films to fully harness the multifunctional potential of these green composite materials.

Challenges and future prospects

There are various challenges, as well as bright applications, associated with the chitosan/PVA/CaO blend system. The outlook is promising because, through optimization of the formulations and processing conditions, multi-purpose, biodegradable materials with regulated bio-minerality, prolonged antibacterial properties and high mechanical properties can be formed.

Techniques such as advanced surface modifications, nano-dispersion methods and life cycle analysis could expand the potential applications of these materials in water treatment, agriculture, and eco-friendly packaging.

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Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this article.

References

1. Hasan S, Boddu VM, Viswanath DS, Ghosh TK. Chitin and Chitosan: Science and Engineering. Cham: Springer Nature Switzerland AG; 2022. https://doi.org/10.1007/978-3-031-01229-7
2. Levengood SKL, Zhang M. Chitosan-based scaffolds for bone tissue engineering. J Mater Chem B. 2014;2(21):3161-3184. https://doi.org/10.1039/c4tb00027g
3. Bharadwaz A, Jayasuriya AC. Recent trends in the application of widely used natural and synthetic polymer nanocomposites in bone tissue regeneration. Mater Sci Eng C Mater Biol Appl. 2020;110:110698. https://doi.org/10.1016/j.msec.2020.110698
4. Dhandayuthapani B, Yoshida Y, Maekawa T, Kumar DS. Polymeric scaffolds in tissue engineering application: a review. Int J Polym Sci. 2011;2011:290602. https://doi.org/10.1155/2011/290602
5. Abdelghany AM, Menazea AA, Ismail AM. Synthesis, characterization and antimicrobial activity of Chitosan/Polyvinyl Alcohol blend doped with Hibiscus Sabdariffa L. extract. J Mol Struct. 2019;1197:603-609. https://doi.org/10.1016/j.molstruc.2019.07.089
6. Mata GCD, Morais MS, Oliveira WPD, Aguiar ML. Composition effects on the morphology of PVA/chitosan electrospun nanofibers. Polymers (Basel). 2022;14(22):4856. https://doi.org/10.3390/polym14224856
7. Hassan CM, Peppas NA. Structure and applications of poly(vinyl alcohol) hydrogels produced by conventional crosslinking or by freezing/thawing methods. In: Biopolymers· PVA Hydrogels, Anionic Polymerisation Nanocomposites. Berlin: Springer; 2000:37-65. https://doi.org/10.1007/3-540-46414-X_2
8. Rafique A, Zia KM, Zuber M, Tabasum S, Rehman S. Chitosan functionalized poly(vinyl alcohol) for prospects biomedical and industrial applications: A review. Int J Biol Macromol. 2016;87:141-154. https://doi.org/10.1016/j.ijbiomac.2016.02.035
9. Bi S, Pang J, Huang L, Sun M, Cheng X, Chen X. The toughness chitosan-PVA double network hydrogel based on alkali solution system and hydrogen bonding for tissue engineering applications. Int J Biol Macromol. 2020;146:99-109. https://doi.org/10.1016/j.ijbiomac.2019.12.186
10. Hezma AM, Rajeh A, Mannaa MA. An insight into the effect of zinc oxide nanoparticles on the structural, thermal, mechanical properties and antimicrobial activity of Cs/PVA composite. Colloids Surf A Physicochem Eng Asp. 2019;581:123821. https://doi.org/10.1016/j.colsurfa.2019.123821
11. Algadi H, Alhoot MA, Yaaqoob LA. Systematic review of antibacterial potential in calcium oxide and silicon oxide nanoparticles for clinical and environmental infection control. J Appl Biomed. 2025;23(1):1-15. https://doi.org/10.32725/jab.2025.001
12. Fatima F, Siddiqui S, Khan WA. Nanoparticles as novel emerging therapeutic antibacterial agents in the antibiotics resistant era. Biol Trace Elem Res. 2021;199(7):2552-2564. https://doi.org/10.1007/s12011-020-02394-3
13. Alobaidi YM, Ali MM, Mohammed AM. Synthesis of Calcium Oxide Nanoparticles from Waste Eggshell by Thermal Decomposition and their Applications. Jordan J Biol Sci. 2022;15(2):235-242.
14. Adaikalam K, Hussain S, Anbu P, Rajaram A, Sivanesan I, Kim HS. Eco-Friendly Facile Conversion of Waste Eggshells into CaO Nanoparticles for Environmental Applications. Nanomaterials (Basel). 2024;14(20):1620. https://doi.org/10.3390/nano14201620
15. Sutharsan M, Senthil Murugan K, Narayanan K, Natarajan TS. Chitosan/Polyvinyl Alcohol/g-C3N4 Nanocomposite Film: An Efficient Visible Light-Responsive Photocatalyst and Antimicrobial Agent. Processes. 2025;13(1):229. https://doi.org/10.3390/pr13010229
16. Lishchynskyi O, Stetsyshyn Y, Raczkowska J, Awsiuk K, Orzechowska B, Abalymov A, et al. Fabrication and impact of fouling-reducing temperature-responsive POEGMA coatings with embedded CaCO3 nanoparticles on different cell lines. Materials (Basel). 2021;14(6):1417. https://doi.org/10.3390/ma14061417
17. Wang J, Zhuang S. Chitosan-based materials: Preparation, modification and application. J Clean Prod. 2022;355:131825. https://doi.org/10.1016/j.jclepro.2022.131825
18. Lewandowska K, Szulc M. Rheological and film-forming properties of chitosan composites. Int J Mol Sci. 2022;23(15):8763. https://doi.org/10.3390/ijms23158763
19. Rahman Khan MM, Rumon MMH, Islam M. Synthesis, Rheology, Morphology, and Mechanical Properties of Biodegradable PVA-Based Composite Films: A Review on Recent Progress. Processes. 2024;12(12):2815. https://doi.org/10.3390/pr12122880
20. Sun Y, Zhang W, Li J, Han R, Lu C. Mechanism and performance analysis of nanoparticle-polymer fluid for enhanced oil recovery: A review. Molecules. 2023;28(11):4331. https://doi.org/10.3390/molecules28114331
21. Szymańska E, Winnicka K. Stability of chitosan-a challenge for pharmaceutical and biomedical applications. Mar Drugs. 2015;13(4):1819-1846. https://doi.org/10.3390/md13041819
22. Ormazábal E, Moreno-Serna V, Sepúlveda FA, Loyo C, Ortiz JA, Melo F, et al. Antimicrobial nanocomposites based on biowaste eggshell derived CaO nanoparticles for potential food packaging application. Food Bioprod Process. 2024;148:123-135. https://doi.org/10.1016/j.fbp.2024.09.003
23. Falsafi SR, Rostamabadi H, Assadpour E, Jafari SM. Morphology and microstructural analysis of bioactive-loaded micro/nanocarriers via microscopy techniques; CLSM/SEM/TEM/AFM. Adv Colloid Interface Sci. 2020;280:102166. https://doi.org/10.1016/j.cis.2020.102166
24. Muhd Julkapli N, Akil HM, Ahmad Z. Preparation, properties and applications of chitosan-based biocomposites/blend materials: a review. Compos Interfaces. 2011;18(6):449-507. https://doi.org/10.1163/156855411X610232
25. Heidari M, Mousavi SB, Rahmani F, Sene RA. Eco-friendly, sustainable and porous eggshell/tea waste-derived CaO nanoparticles as a high-temperature CO2 sorbent: Fabrication and textural/morphological evaluation. J Ind Eng Chem.

2024;134:169-180. https://doi.org/10.1016/j.jiec.2023.12.048
26. Kou SG, Peters LM, Mucalo MR. Chitosan: A review of sources and preparation methods. Int J Biol Macromol. 2021;169:85-94. https://doi.org/10.1016/j.ijbiomac.2020.12.005
27. Chopra H, Bibi S, Kumar S, Khan MS, Kumar P, Singh I. Preparation and evaluation of chitosan/PVA based hydrogel films loaded with honey for wound healing application. Gels. 2022;8(2):111. https://doi.org/10.3390/gels8020111
28. Grande-Tovar CD, Castro Castro JI, Barba-Rosado LV, Zapata PA, Insuasty D, Valencia-Llano CH. Histology Assessment of Chitosan-Polyvinyl Alcohol Scaffolds Incorporated with CaO Nanoparticles. Molecules. 2025;30(2):276. https://doi.org/10.3390/molecules30020276
29. Sariyerli GS, Sakarya O, Akcadag UY. Comparison tests for the determination of the viscosity values of reference liquids by capillary viscometers and stabinger viscometer SVM 3001. Int J Metrol Qual Eng. 2018;9:7. https://doi.org/10.1051/ijmqe/2018004
30. Nokhasteh S, Molavi AM, Khorsand-Ghayeni M, Sadeghi-Avalshahr A. Preparation of PVA/Chitosan samples by electrospinning and film casting methods and evaluating the effect of surface morphology on their antibacterial behavior. J Polym Res. 2019;26(8):196. https://doi.org/10.1088/2053-1591/ab572c