UDK 62-112.5:338.439.54:658.788
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
Mater. Tehnol.

BIOPOLYMER COMPOSITE FILMS BASED ON HYDROXYPROPYL METHYLCELLULOSE (HPMC) AND PECTIN REINFORCED WITH MgO AND ZnO NANOPARTICLES FOR STRAWBERRY (*Fragaria vesca*) PRESERVATION

BIOPOLIMERNI KOMPOZITNI FILMI NA OSNOVI HIDROKSIPROPIL METILCELULOZE IN PEKTINA, OJAČANI Z NANO OKSIDNIMI DELCI MAGNEZIJEVEGA IN CINKOVEGA OKSIDA KOT PREVLEKA ZA ZAŠČITO JAGOD

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Prejem rokopisa – received: 2025-10-07; sprejem za objavo – accepted for publication: 2026-03-30

doi:10.17222/mit.2025.1586

Biopolymers have been widely investigated as an alternative to synthetic plastics. Perishable foods such as fruits and vegetable products have a short shelf life and cause significant postharvest losses, posing a major challenge to the food supply chain. In this research, hydroxypropyl methylcellulose (HPMC)/pectin composite reinforced with 0.5 % magnesium oxide nanoparticles (MgO NPs) and 0.5 % zinc oxide nanoparticles (ZnO NPs) was investigated. The purpose of developing these materials is to improve the mechanical and barrier properties of biopolymer composite films and consider them as an alternative to synthetic plastics of fossil origin. The aim of this study was to create and characterize novel eco-friendly biopolymer composite films for the preservation of strawberries. However, strawberries are highly perishable and susceptible to physical and microbial deterioration after harvest. Their shelf life was extended using a nanocomposite coating based on an HPMC/pectin biopolymer matrix reinforced with MgO and ZnO nanoparticles. Coated and uncoated strawberries were monitored for 10 days at 20 °C. The HPMC/pectin/NPs coating acted as a physical barrier, reducing respiration rate, weight loss, and preserving the good shape of strawberries (*Fragaria vesca*) compared to uncoated fruits during storage. In addition, the results showed that nanocomposite films prepared from HPMC/pectin/NPs provided excellent bacterial inhibition against *Escherichia coli* and *Staphylococcus aureus*, making them suitable for food packaging. Moreover, the addition of MgO and ZnO NPs significantly increased the flexibility and plasticity of the nanocomposite films compared to HPMC/pectin films alone. In short, the use of an active nanocomposite coating of HPMC/pectin/MgO NPs and/or ZnO NPs can be considered an effective method to protect strawberries from physical and biological damage during storage and transportation.

Key words: hydroxypropyl methylcellulose (HPMC), pectin, zinc oxide nanoparticles, magnesium oxide nanoparticles, nanocomposite coating, food packaging

Biopolimere so raziskovalci v preteklosti že veliko raziskovali kot alternativo sintetični plastiki. Pokvarljiva živila, kot so sadje in zelenjava, imajo kratek rok trajanja in povzročajo znatne izgube po žetvi oziroma pobiranju. To predstavlja velik izziv za prehransko verigo. V tem članku avtorji opisujejo raziskavo biopolimernega kompozita na osnovi hidroksipropil metilceluloze (HPMC)/pektina, ojačanega z 0,5 % nanodelcev magnezijevega oksida (MgO NP) in 0,5 mas. % nanodelcev cinkovega oksida (ZnO NP). Namen razvoja teh materialov je bil izboljšati mehanske in pregradne lastnosti biopolimernih kompozitnih filmov, da bi jih lahko obravnavali kot alternativo sintetični plastiki fosilnega izvora. Cilj avtorjev je bil ustvariti in okarakterizirati nove okolju prijazne biopolimerne kompozitne filme za konzerviranje jagod. Vendar so jagode zelo pokvarljive in dovzetne za fizično in mikrobno kvarjenje po nabiranju. V tem primeru so podaljšali rok trajanja užitnosti jagod z metodo nanašanja nanokompozitnega premaza iz biopolimerne matrice na osnovi HPMC/pektina, ojačane z nanodelci MgO in ZnO. Jagode brez in s prevleko so avtorji 10 dni spremljali med skladiščenjem pri sobni temperaturi (20 °C). Prevleke na plodovih, prevlečenih s HPMC/pektinom/NP, so delovale kot fizična ovira, saj so zmanjšale hitrost dihanja, izgubo na masi in ohranile dobro obliko jagod (lat. Fragaria Vesca) v primerjavi z neprevlečenimi jagodami. Poleg tega so rezultati pokazali, da nanokompozitni filmi, pripravljeni iz HPMC/pektina/NP, zagotavljajo odlično proti bakterijsko oviro za Escherichia coli in Staphylococcus aureus. Zato so primerne za pakiranje živil. Poleg tega je dodatek nanodelcev MgO in ZnO znatno povečal prožnost in plastičnost nanokompozitnih filmov v primerjavi s samo HPMC/pektinskim filmom. Avtorji v pričujočem članku torej ugotavljajo, da se uporaba aktivnega nanokompozitnega premaza iz HPMC/pektina/MgO NP in/ali ZnO NP lahko smatra kot učinkovita metoda za zaščito jagod pred fizičnimi in biološkimi poškodbami med skladiščenjem in transportom.

Ključne besede: hidroksipropil metilceluloza (HPMC), pektin, cinkov nanooksid, magnezijev nanooksid, nanokompozitni premaz, embaliranje živil

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1 INTRODUCTION

Fruits and vegetables hold a crucial position in nutritious human diets and rank highly on the hierarchy of consumer interests.[1] Fruits are the living components of a plant that undergo a continuous process of changes in their physical, chemical, biochemical, and sensory characteristics as they grow, develop, and mature. Even after harvest, fruits and vegetables still undergo respiration, and the longevity of their shelf-life diminishes with a heightened respiration rate.[2] These effects are also severe in non-climacteric fruits such as grapes, citrus fruits, and strawberries, which are characterized by high perishability and rapid quality deterioration after harvest. Although they do not exhibit a significant increase in respiration rate driven by ethylene, they remain highly susceptible to microbial spoilage, water loss, and mechanical damage. The peel and skin of fruits and vegetables serve as protective barriers; any damage occurring during harvesting and postharvest handling disrupts natural gas exchange, increases water and flavor losses, and raises the risk of microbial spoilage. In particular, the fragile skin of strawberries acts as a primary barrier against pathogens and dehydration; any injury during harvesting or handling significantly increases their susceptibility to rapid senescence, excessive softening, and reduced shelf life.[3] Synthetic-plastic based packaging materials are extensively employed in food packaging due to their advantageous mechanical and barrier characteristics. On the other hand, their non-biodegradable nature results in considerable solid waste accumulation, presenting a significant risk to the environment. In recent years, the exploration of disposable packaging materials derived from natural biopolymers has been carried out. Researchers have examined a range of natural biopolymers, such as pectin (PEC), alginate, chitosan, starch, gelatin, hydroxypropyl methylcellulose (HPMC), and gluten, for the production of edible films and coatings at a laboratory scale. However, their insufficient mechanical and barrier properties restrict their feasibility as substitutes for synthetic packaging materials.

Among these biopolymers[4] pectin (PEC), which is a linear water-soluble polysaccharide primarily present in citrus peel and apple pomace, serves as an essential part of plant cell walls, and it possesses significant nutritional and functional characteristics for use in food as either a food additive and/or a processing aid, including functions as a gelling and thickening agent.[5] In recent years pectin has been a popular biopolymer used for fabrication of active composite films, formulation of edible food coating,[6] and as an attractive film-forming material for edible packaging. It has been widely used due to its low cost, availability, biodegradability, non-toxicity, and biocompatibility. Nonetheless, films based on pure pectin have some disadvantages, such as weak chemo-physical characteristics and unsatisfactory mechanical performances, which limit their use in practical packaging applications.[7] Pectin is also a suitable component for improving the antibacterial properties and water resistance of other polymer films. The presence of a hydrophilic polysaccharide fraction that offers high steric stabilization and a hydrophobic protein or phenolic fraction allows pectin to stabilize emulsions under a variety of environmental stimuli. Pectin also possesses certain antioxidant properties, which are directly linked to the presence of hydroxyl groups. Moreover, hydrogen bonding interactions between the carboxylate and/or hydroxyl groups of pectin and other polysaccharides are anticipated to take place, helping to create a denser, more compact matrix with better qualities, according to Yi Liu et al. (2024).[8] Therefore, the development of edible films based on pectin in combination with other biopolymers has become a research hotspot in recent years; on the other hand, hydroxypropyl methylcellulose (HPMC) may be regarded as a more advantageous option among biopolymers for edible film or coating applications. It is a derivative of cellulose, wherein some of the hydroxyl groups are replaced by hydroxypropyl groups (–CH_3CH (OH) CH2) and methyl groups (–CH_3). It is the most extensively utilized biopolymer matrix for controlled release mechanisms owing to its availability, biocompatibility, water solubility, and non-toxic nature. It demonstrates solubility in cold water as well as in select organic solvents (ethanol and methanol). The solution maintains stability across a broad pH range (2–12) and exhibits superior moisture barrier properties compared to other polysaccharides.[9] However, HPMC is limited by its low mechanical strength, poor barrier characteristics, and high susceptibility to environmental conditions. In order to improve its properties, a formulation including both pectin (carboxyl groups) and HPMC (hydroxyl groups) is being prepared where the carboxyl groups of pectin may interact with the hydroxyl groups of HPMC via hydrogen bonding. This interaction can change the viscosity, gel strength, and texture of the final combination. It may influence the porosity and stability of the gel network.[10]

Researchers studied and developed polymer composite systems. They suspected that adding inorganic components to polymers would improve their characteristics. Nanoparticles have been shown to impact the characteristics of basic polymers.[11] Bionanocomposites are hybrid materials composed of biopolymers and inorganic solids, with at least one nanoscale dimension. Bionanocomposites are an emerging field of research for both polymer scientists and nanotechnologists, and they are believed to be highly promising for present and future applications because they exhibit multidimensional properties such as biodegradability, biocompatibility, antimicrobial, sensing ability, optical, mechanical, and gas barrier properties.[12] Materials based on nanoscale metal oxides provide a solution to current and future technological challenges due to their novel features. Magnesium oxide (MgO) is regarded as a highly useful substance in both basic and applied research. Furthermore, due to its simple stoichiometry, high ionic characteris-

tics, and crystalline structure, it is regarded as a unique material capable of forming a wide range of particle shapes and sizes.[13] The incorporation of zinc oxide nanoparticles (ZnO NPs) in biopolymer-based films significantly enhances the mechanical properties and barrier properties of the films. ZnO NPs increase the tensile strength (TS) and decrease the water vapor permeability (WVP) of biopolymer films. Furthermore, ZnO NPs do not have a significant effect on the flexibility of biopolymer films, although agglomerations may occur at higher concentrations of ZnO NPs.[14] However, regarding strawberries, to the best of our knowledge, there are no reports on the effect of biocomposite films based on HPMC/pectin, reinforced with MgO nanoparticles and ZnO nanoparticles. As a result, the characteristics of HPMC films with incorporated pectin, MgO and ZnO nanoparticles was studied to examine the mechanical properties, water vapor permeability, physicochemical properties, and rheological properties of the films and their applications in strawberry packaging and preservation.

2 EXPERIMENTAL PART

2.1 Materials

Hydroxypropyl methylcellulose (hydroxypropyl content of ≈10 %, methyl content of ≈29 %, degree of substitution of 1.4, average degree of polymerization of 750) was purchased from Shandong Heda Co., Ltd. Glycerol was obtained from Yongda Chemical Reagent Co., Ltd. (Tianjin, China). Pectin (≥74.0 % dried basis, ≤10 % moisture, degree of esterification (DE) of 58.3 %) was purchased from Sigma Co., Ltd. (Shanghai, China). ZnO powder (particle size of 50≈100 nm, > 99 %) was obtained from L'Urederra technological centre (Spain). MgO powder (particle size of 50≈100 nm, > 99 %) was obtained from L'Urederra technological centre (Spain).

2.2 Composite film elaboration

Various methods are employed for the fabrication of polymer-based films, among which casting, spraying, and extrusion are the most prevalent techniques, as illustrated in Figure 1. Our films were prepared using the casting method in a manner similar to that reported by Jean-Marie Raquez et al. in 2013,[15] with slight modifications. HPMC was dissolved in water and stirred using a magnetic stirrer at 100 rpm at 20 °C for 24 hours to prepare a 2 % HPMC solution while minimizing air bubbles. Separately, 1.5 % of pectin was dissolved in distilled water at 20 °C for 2 hours at 100 rpm until a homogeneous solution was obtained. The pectin solution was then added to the HPMC solution, followed by the addition of glycerol (20 % of dry matter) as a plasticizing agent. The resulting mixture was gently stirred until a clear solution was obtained. The final mixture was then supplemented with ZnO NPs or MgO NPs dispersed in distilled water at a concentration of 0.5 % dry matter to formulate bionanocomposite film-forming solutions (FFS).

3 CHARACTERIZATIONS

3.1 Physicochemical properties of films

3.1.1 Measurement of film thickness

The thickness of the prepared film was measured at three different locations using a digital vernier calliper micrometer (aerospace LCD digital vernier caliper, 150 mm), and the average thickness was calculated.

3.1.2 Biodegradation test

The biodegradability of the samples was evaluated by measuring the mass loss of the compounds as a function of time in a composting environment. The samples are weighed and placed in a compost bin at a depth of 12–15

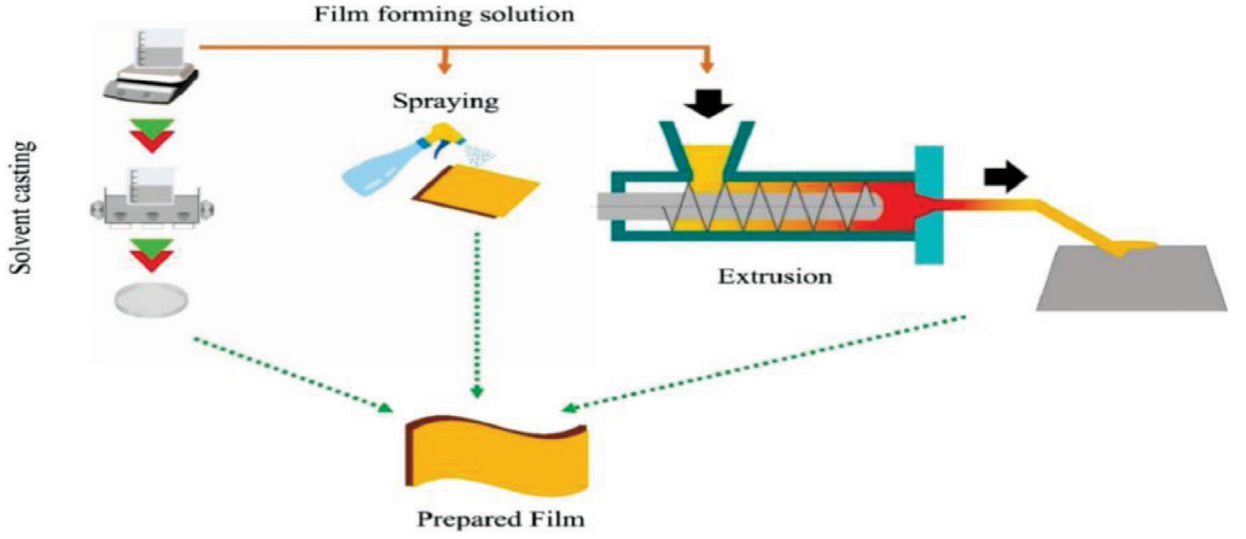

Figure 1: Schematic representation of various film-forming processes[16]

cm. They were left there for 10 days.[17] The mass loss was calculated according to the following formula:

$$\text{Mass loss (\%)} = \frac{mi - mf}{mi} \times 100 \quad (1)$$

With:
mi: initial mass of the tested sample
mf: final mass of the tested sample

3.1.3 Humidity level

After preparing various formulations, the samples are weighed and recorded (m_0) before being placed in the oven. Drying continued for about 48 hours until completion. Moisture levels were determined according to standard NF M 03-002.

$$H\ (\%) = \frac{m0 - mf}{m0} \times 100 \quad (2)$$

3.2 Structural properties determined using FT-IR

FTIR-ATR spectra were recorded by an Agilent Cary 630 FTIR spectrometer. Measurements were performed in a range of 4000–650 cm^{-1}, using solid film samples, with data acquisition via IRsolution software. The obtained spectra were used to determine interactions within the film matrix.

3.3 Mechanical properties and water vapor permeability

In a tensile test, a standardized specimen is subjected to uniaxial stress until rupture in order to determine the mechanical properties of the material, such as tensile strength, elongation at break, and elastic limit.[18,19] Tests were carried out at room temperature on standardized film specimens with dimensions of (30 × 50 × 0.05) mm. The mechanical properties of the films were influenced by both the fabrication method and formulation.

The tensile properties were evaluated using a universal testing machine (maximum load capacity of 600 kN). Prior to testing, samples were preconditioned under controlled conditions. The specimens were then subjected to a constant crosshead speed of 1 mm/min until rupture. Stress–strain curves were automatically recorded, and force, *F*(N), was measured as a function of elongation, ΔL (mm), allowing the determination of tensile strength, elongation at break, and elastic modulus,[18] calculated from the maximum stress at break, δ(MPa):

(3)

With:
S: initial cross-sectional area of the test tube (m^2), equal to the product of its thickness and width
F_{max}: maximum force at break (N)

Young's modulus (MPa) corresponds to the slope of the linear part of the stress–strain curve at small deformations.

$$E = \frac{\delta}{\varepsilon} \quad (4)$$

With:
δ: stress (N/m^2 or MPa) and ε: deformation (%)

The percentage of nominal deformation (elongation) of the film at the breaking point corresponds to the ratio between elongation and the initial reference length.

$$\varepsilon = \frac{\Delta l}{l_0} \times 100 \quad (5)$$

With:
$\Delta L = l - l_0$: lengthening at break (mm)
l_0: initial length of test tube
L: final length of test tube

3.4 Water vapor permeability (WVP)

Water vapour permeability (WVP) is defined as the amount of water vapor transmitted through a unit area of film per unit time under specified conditions. Circular specimens were cut from dried film sheets. For sample preparation, glass vials containing distilled water were covered with film samples and sealed using silicone rings and aluminum caps to ensure airtight conditions. The initial weight of each vial was recorded before being placed in a desiccator maintained at 58 % relative humidity or low relative humidity (approximately 0 %).

The samples were kept at a controlled temperature for 72 h and weighed at predetermined time intervals.[20]

$$\text{WVP} = \frac{w \cdot l}{A \cdot t \cdot \Delta P} \quad (6)$$

Where:
W: weight loss (g)
L: film thickness (mm)
A: area (cm^2)
t: time (h)
ΔP = vapor pressure difference across the film (Pa)

3.5 Scanning electron microscopy analysis

Scanning electron microscopy (SEM) analyses were carried out using a Philips CM120 Biofilter apparatus with a TEM module at an acceleration voltage of 120 kV. Raw MgO nanoparticles were analyzed by depositing a droplet of nanoparticle suspension (0.1 % w/w in distilled water) on an aluminum-coated grid. The MgO dispersion within the HPMC matrix was evaluated using ultrathin sections of the nanocomposites.

3.6 Rheological behavior

All rheological analyses were performed using a controlled stress rheometer (MCR 302, Anton Paar Physical, and GmbH, Germany) with parallel-plate geometry (gap of 0.5 mm and diameter of 25 mm). The experimental results were processed using Rheoplus US200 software (Anton Paar, GmbH, Germany). Film-forming solutions

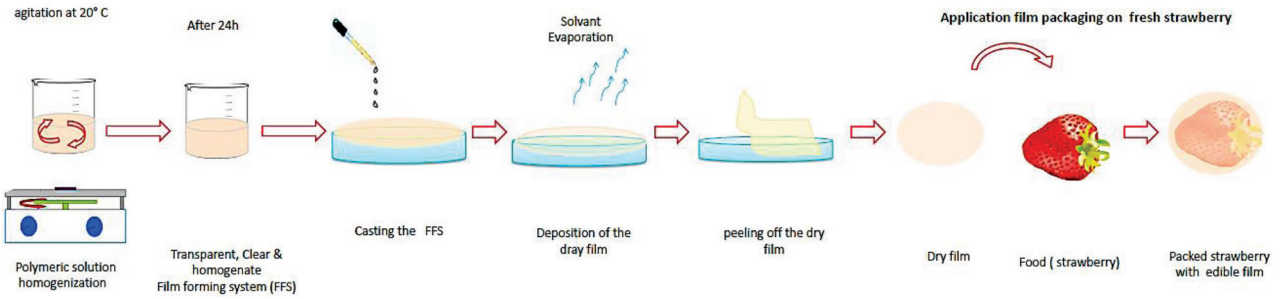

Figure 2: Schematic of the casting method for applying film coating to strawberries

were analyzed at 20 °C under controlled shear rate. The structural model of Carreau, used to characterize the flow behavior of polymer dispersions and other shear-thinning fluids, was then used to determine and modify their experimental flow curves, which expressed the evolution of the apparent viscosity with the shear rate ($\eta_{app} = f(\gamma)$).[21]

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{(1 - k\gamma)^{2p}} \quad (7)$$

The viscous behavior of the film-forming solutions (FFS) at zero shear rates is expressed by the parameter η_0, which stands for zero shear viscosity. The film-forming solutions (FFS) were analyzed at 20 °C in oscillation shear mode at a frequency of 1 Hz. In contrast, η_∞ is the infinite shear viscosity, which expresses the behavior of a suspension when it is subjected to extreme shear; K is a time constant and P is an exponent for the determination of the viscoelastic properties. The conservation (storage) modulus (G') and loss modulus (G''), two viscoelastic parameters, were assessed. The linear-viscoelastic range (LVE range) was used to infer their values, which were designated as G' at LVE and G'' at LVE.[22]

4 USE OF THE NANOCOMPOSITE FOR STRAWBERRY PRESERVATION

Mature strawberries (*Fragaria vesca*) were obtained at a local fruit store in Blida city (altitude of 229 m), Algeria. Strawberries of equal size, weight, and maturity were pretreated by washing with distilled water and blow-drying at room temperature, at 20 °C, as shown in **Figure 2**. The fruits were divided into five lots: uncoated strawberries, strawberries coated with HPMC, HPMC/PEC, HPMC/PEC/0.5% ZnO NPs, and HPMC/PEC/0.5% MgO NPs films. They were then kept at 25 °C. The appearance and physicochemical parameters of coated and untreated fruits were measured every day for 10 days.

4.1 Determination of pH

The pH of all strawberry samples including the uncoated control group, and coated-fruit groups was measured using a digital pH meter (InoLab pH 7110-1AA112, Germany). Measurements were performed in five replicates for each treatment.

4.2 Weight loss

Weight loss of strawberries with and without coating was evaluated using a digital balance. Fruits were weighed at the beginning of storage at 25 °C and marked as m_0. During storage, fruits were daily weighed and noted as m_i. The experiments were run in five replicates during each treatment. The weight loss (%) was calculated as follows:

$$\text{Weight loss (\%)} = \frac{m0 - mi}{m0} \times 100 \quad (8)$$

4.3 Titratable acid

The titratable acid content was determined with the titration method (Dou, Shi, & Li, 2020). The strawberry pulp was homogenized and heated in a boiling-water bath for 30 min. After cooling, 1 mL of filtrate, 5 mL of water and 3 drops of 1 % phenolphthalein indicator were mixed and titrated with 0.01 mol/L sodium hydroxide (NaOH) until a reddish color was obtained. The results were expressed as mass fraction (%).[23]

4.4 Microbiological study of strawberry preservation

Strawberries were tested for their antibacterial properties against *Bacillus cereus* (BC), *Staphylococcus aureus* (SA), and *Escherichia coli* (EC). Coated and uncoated strawberries were cut into tiny pieces and weighed in order to make a strawberry extract sample. The pieces were mixed and 70 % ethanol was added at a weight-to-volume ratio of 1:10. The mixture was macerated at room temperature in the dark for 24 h. Whatman paper was used to filter the extract, which was then kept at 4 °C until it was needed.

The studied bacteria included *Escherichia coli*, *Staphylococcus aureus*, and *Bacillus cereus*. Each strain was grown overnight on Mueller-Hinton nutrient agar and Sabouraud agar. For every test, a bacterial suspension equivalent to a 0.5 McFarland standard, approximately 10^8 CFU/mL, was created. Afterward, the disk diffusion method was employed by infusing 20 to 30 µL

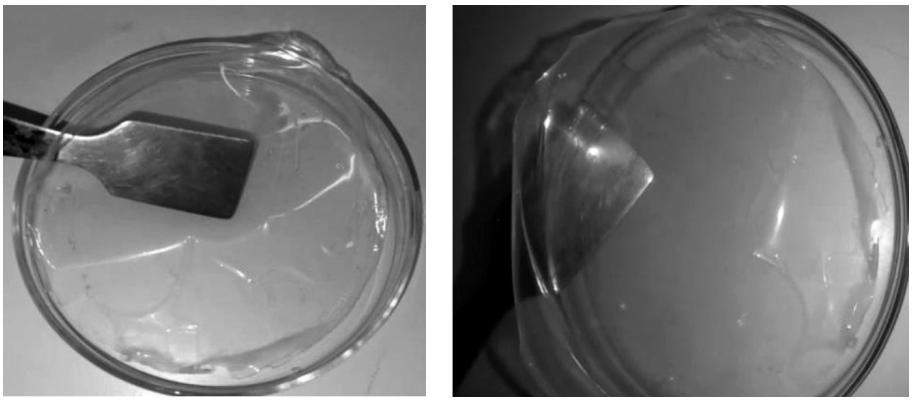

Figure 3: Visual appearance of the prepared biopolymer films

of strawberry extract onto 6 mm paper discs. The bacteria were spread evenly on the Mueller-Hinton and Sabouraud plates. The soaked discs were placed on the surface of these plates, and kept there at 37 °C for 24 h.

The antibacterial properties are evaluated by measuring the area where bacteria cannot grow and by measuring its effectiveness in millimeters. To find the minimum inhibitory concentration (MIC), a series of two-fold dilutions of the strawberry extract was prepared in broth. Each well of a 96-well microplate received 100 µL of each dilution together with 100 µL of bacterial suspension. Following a 24-hour incubation period at 37 °C, a viability indicator such as TTC was introduced. The MIC is defined as the lowest dilution that prevents any visible bacterial growth, marked by an absence of color change. The study incorporated a negative control with only the solvent (ethanol), a positive control using a standard antibiotic such as ampicillin or gentamicin, and a blank control containing media without bacteria. These control samples were essential for confirming the accuracy of the experimental outcomes.[24]

5 RESULTS AND DISCUSSION

The different biocomposite films obtained exhibited a homogeneous, thin, transparent, flexible appearance as shown on **Figure 3**.

5.1 Physicochemical properties of films

The thickness of the films is influenced by the composition of the film-forming system (FFS), as well as by the viscosity. As a result, HPMC-based films are thicker than the composite films (HPMC/PEC) and their reinforced variants. The biodegradability test indicates that the biocomposite films were degraded approximately twice as much as the HPMC films. On the other hand, the incorporation of pectin resulted in increased stickiness of the films.

The addition of MgO nanoparticles (0.7 %) or ZnO nanoparticles (0.5 %), which showed better results compared to other concentrations, considerably enhanced the biodegradability of the films, making them a more environmentally friendly option. Conversely, **Table 1** also shows that the moisture content increases with the addition of pectin and nanoparticles to the HPMC matrix up to 0.7 % of MgO or ZnO nanoparticles; beyond this concentration, it decreases. These findings indicate that nanoparticles have a significant influence on the properties of HPMC films.

Table 1: Thickness, mass loss percentage, and moisture content (H) of the developed HPMC, PEC, and nanocomposite-based biopolymer films

Samples	Thickness, mm	Mass loss, %	H, %
HPMC	0.04 ± 0.01	15.02	13.03
PEC	0.02 ± 0.01	22.64	20.44
HPMC/PEC	0.03 ± 0.01	17.67	18.41
HPMC/PEC/MgO	0.03 ± 0.01	25.75	15.22
HPMC/PEC/ZnO	0.03 ± 0.01	23.58	17.23

5.2 Structural properties obtained with FT-IR

FTIR spectra of the films (**Figure 4**) show that the broad and intense bands observed at 3314–3332 cm^{-1} and the weak bands at 2885–2932 cm^{-1} correspond to the O–H stretching vibrations of hydroxyl groups and C–H

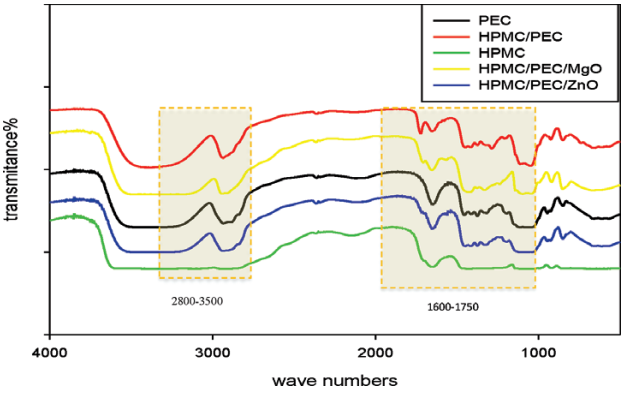

Figure 4: FTIR spectra of the developed biopolymer films: HPMC, PEC, HPMC/PEC, HPMC/PEC/MgO, and HPMC/PEC/ZnO, showing the characteristic functional groups and interactions between components

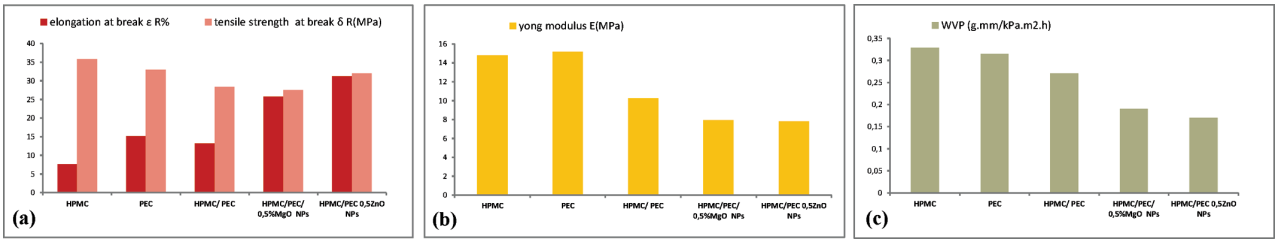

Figure 5: (a,b) Mechanical properties (tensile strength, elongation at break, Young's modulus) of HPMC, HPMC/pectin, HPMC/pectin/ZnO, and HPMC/pectin/MgO films; (c) water vapor permeability (WVP) of the films

stretching vibrations, respectively. Moreover, the strong bands at 1719–1739 cm^{-1} and 1604–1637 cm^{-1} are attributed to the C=O stretching of carboxylic acid (COOH) and amide I, respectively.[25]

The addition of pectin to the HPMC matrix caused a shift in the O–H band from 3339 to 3320 cm^{-1}, indicating enhanced hydrogen bonding interactions between HPMC and pectin, which improved the mechanical strength and barrier properties of the films.

Upon incorporation of MgO and ZnO nanoparticles, no new peaks were observed, suggesting that no covalent bonds were formed between HPMC/pectin and MgO/ZnO nanoparticles. Therefore, the interactions between the components were mainly physical rather than chemical in nature.[26]

5.3 Mechanical and water vapor permeability

Figure 5 summarizes the results for the mechanical and moisture barrier properties of the produced films. It became clear that the incorporation of pectin, MgO NPs, and ZnO NPs affects the mechanical and water vapor permeability (WVP) properties of HPMC. **Figure 5a** shows that the elongation at break significantly increased and the TS decreased. On the other hand, **Figure 5b** clearly shows that Young's modulus, which reflects the stiffness of the material, decreased by over 40 % in the HPMC/pectin film, indicating that the addition of pectin, MgO NPs, and ZnO NPs improved the flexibility of the biopolymer matrix.

WVP is an important characteristic of biodegradable food packaging because it influences food deterioration reactions.[27] As indicated in **Figure 5c**, the trend in WVP was consistent with the mechanical property results. Compared to the HPMC film, HPMC/pectin had lower water vapor permeability. This can be related to the interaction and compatibility of pectin with HPMC, which resulted in more dense and compact films with enhanced water barrier functions. Furthermore, we see that WVP decreased further upon the incorporation of MgO NPs and ZnO NPs films, indicating that the nanocomposite improved the mechanical and barrier properties of the biopolymer matrix due to strong interactions and improved compatibility between its components.

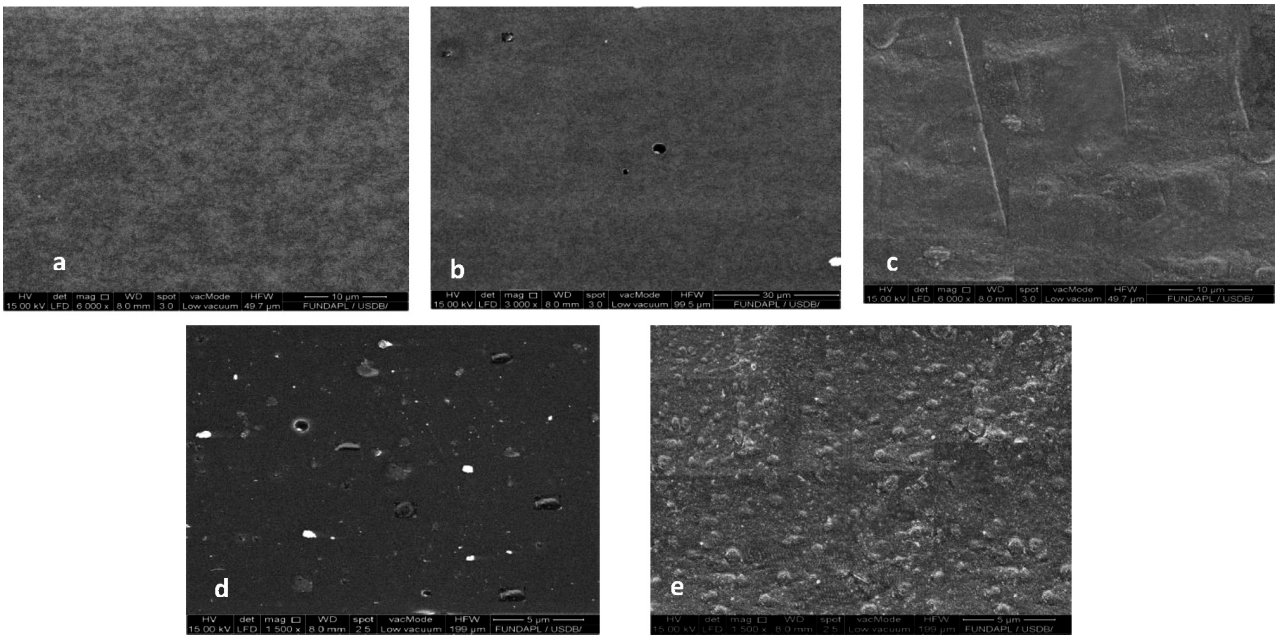

Figure 6: SEM micrographs of the developed films: a) HPMC, (b) pectin, c) HPMC/PEC, d) HPMC/PEC/ZnO, and e) HPMC/PEC/MgO, showing surface morphologies and the effect of nanoparticle incorporation onto the film structure

5.4 Scanning electron microscopy analysis

Figure 6 illustrates the surface morphologies of the films. SEM images indicate that the film samples were all compact and homogenous. In pure HPMC, thin microchannels were observed. The surface and cross-section of the HPMC/pectin film appeared smoother and more compact compared to HPMC, indicating that the hydrogen bond between HPMC and pectin rendered them compatible, as evidenced by the FTIR measurements. Conversely, when NPs (ZnO or MgO) were incorporated, the cross-sections of the films displayed a discontinuous structure with some uniform pores, suggesting that the NPs had been successfully emulsified and uniformly distributed throughout the continuous network of the HPMC/PEC film matrix. While the film containing MgO exhibited larger and fewer aggregates due to their concentration in the matrix, the film incorporating ZnO NPs exhibited relatively smaller nanoscale droplets, with the ZnO NPs uniformly distributed throughout the matrix. This might have resulted in a decline of the film's mechanical properties.

5.5 Rheological behavior

In **Figure 7A**, the progress of the viscoelastic properties, specifically the conservation modulus *G*' and loss modulus *G*", is depicted as a function of strain. This graph reveals two distinct areas: the first one represents the domain of linear viscoelasticity, known as the linear viscoelastic range (LVE range), where both moduli remain constant at low strains, with G' being greater than *G*". In this region, the film exhibits solid viscoelastic behavior, and its deformations are recoverable. The gel point, at which the two modulus values intersect, restricts this area. Following this, there is the second region, where both moduli decrease gradually and *G*" exceeds *G*', suggesting that the HPMC film exhibits liquid characteristics at high deformations which are irreversible. The pectin film exhibits the same rheological behavior as the HPMC film (**Figure 7B**), and the blended HPMC/PEC film displays the same behavior as each polymer individually (**Figure 7C**).

The influence of the NPs (ZnO and MgO) on the HPMC/PEC matrix is evident in the recorded deformations, suggesting that all the biocomposite films (HPMC/PEC/NPs) exhibit typical liquid behavior, characterized by a larger loss modulus (*G*") value compared to the storage modulus (*G*') for all samples (**Figure 7C**). These distortions can also be reversed. However, we can notice that when HPMC and pectin were mixed together, they showed a common flow behavior where the storage modulus (*G*') was greater than the loss modulus (*G*").

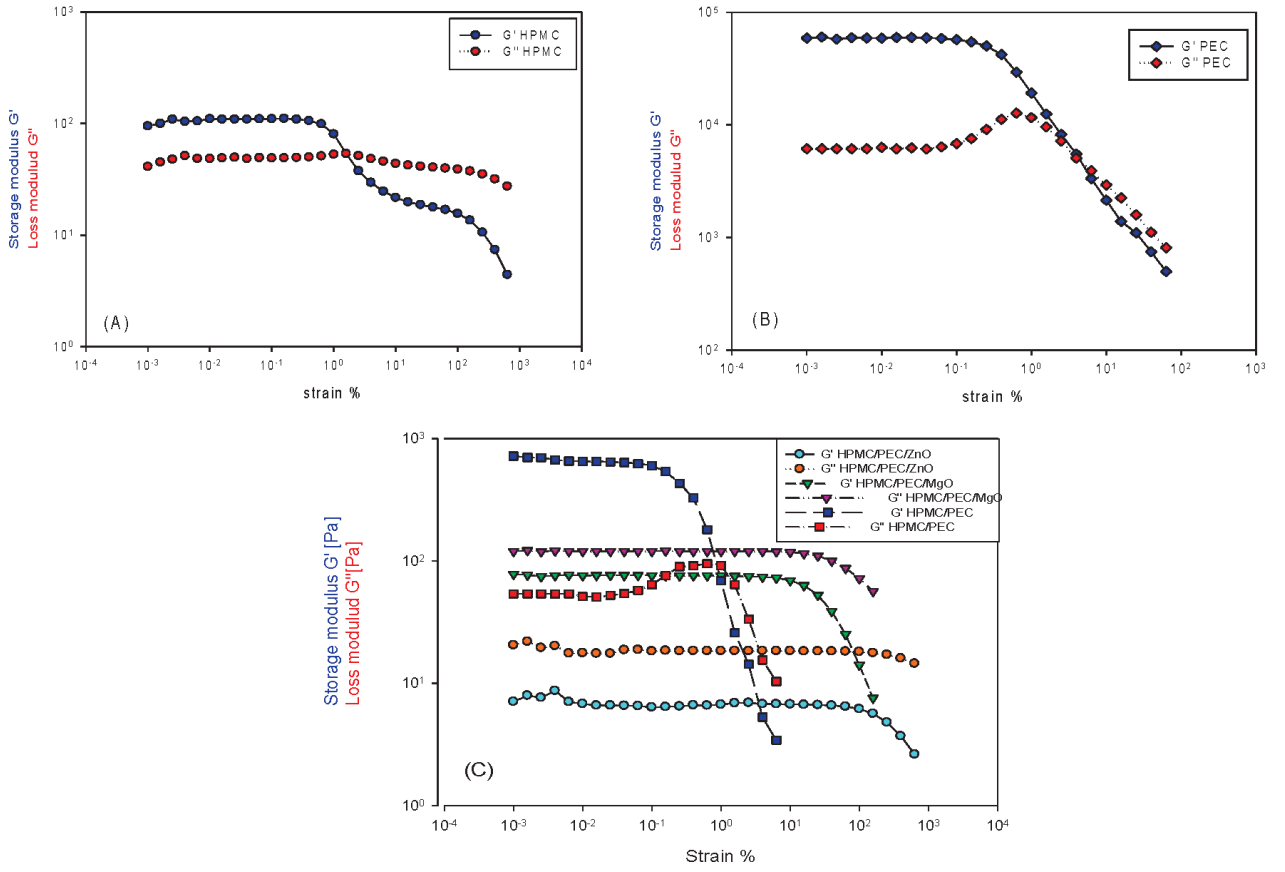

Figure.7: Evolution of the storage modulus (*G*') and loss modulus (*G*") as a function of strain, showing the viscoelastic behavior of (A) HPMC, (B) PEC and (C) HPMC/PEC nanocomposite films

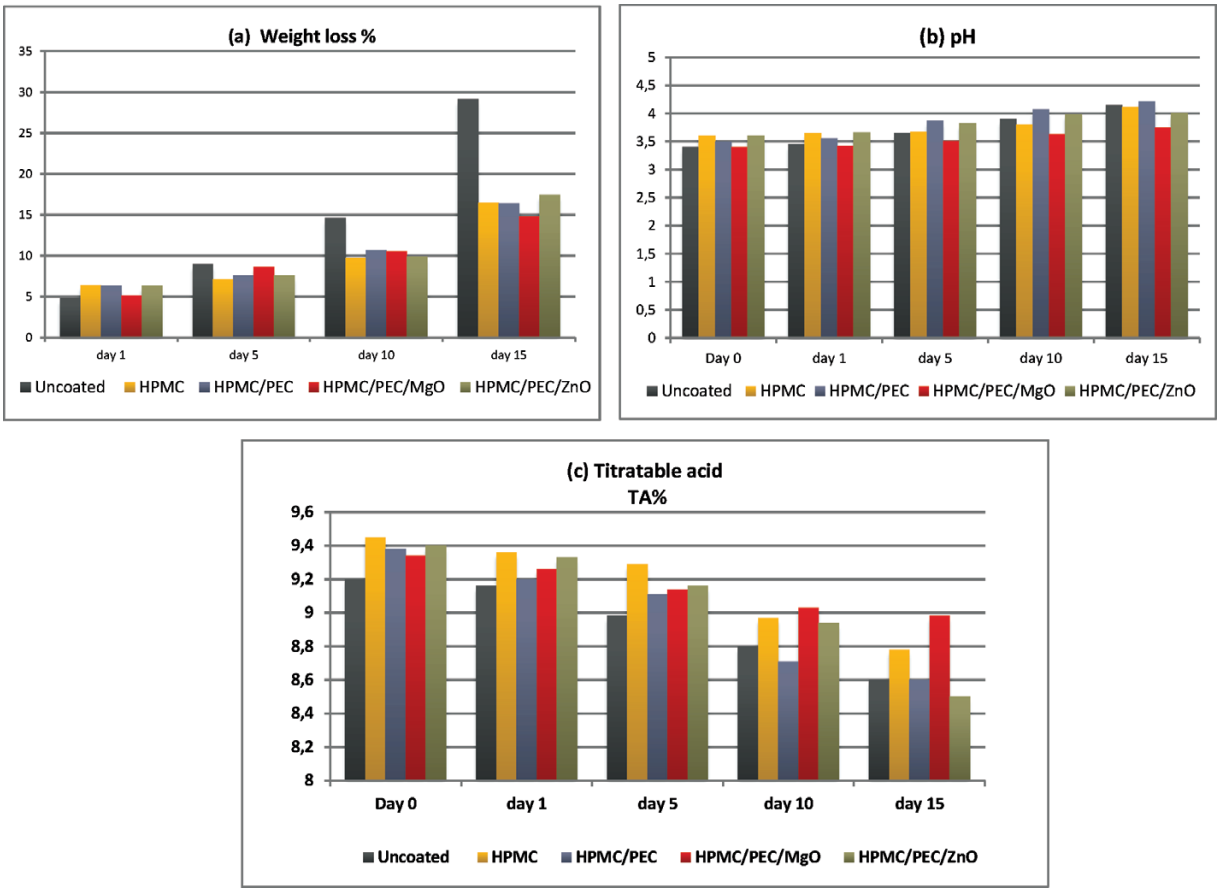

Figure 8: Physicochemical parameters of strawberries: weight, pH, and titratable acidity (TA) of uncoated and coated strawberries during the storage period

This indicates that the mixture was more elastic. However, when we added zinc oxide (ZnO) and magnesium oxide (MgO), this behavior changed. With these metal oxides added, the loss modulus (G'') became larger than the storage modulus (G'), indicating a shift to a more fluid-like behavior. Fourier transform infrared spectroscopy (FTIR) tests revealed that there were no significant chemical reactions taking place, which means the changes we saw were only physical. To sum up, adding ZnO and MgO probably changes how the components interact physically, causing the flow properties to shift from being elastic to more fluid.

6 STRAWBERRY PRESERVATION

6.1 Physicochemical roperties

Figure 8 depicts the physicochemical parameters (weight, pH, titratable acid (TA)) of the strawberries (coated and uncoated). **Figure 8a** demonstrates that uncoated strawberries lost the most weight, 29.16 %, after being stored for 15 d. In contrast, all coated samples showed a significant reduction in weight loss when compared to the control group. Among the various coatings tested, the HPMC/PEC/MgO combination exhibited the best performance, with a weight loss of only 14.82 %, indicating it had a strong moisture barrier and potential antimicrobial properties. As shown in **Figure 8b**, the pH levels of all samples increased over the storage time, reflecting the natural breakdown of acids. The uncoated strawberries saw their pH rise from 3.4 to 4.15, whereas the HPMC/PEC/MgO coated strawberries maintained the highest level of stability, with the final pH of 3.75. This stability implies a delayed aging process and reduced mi-

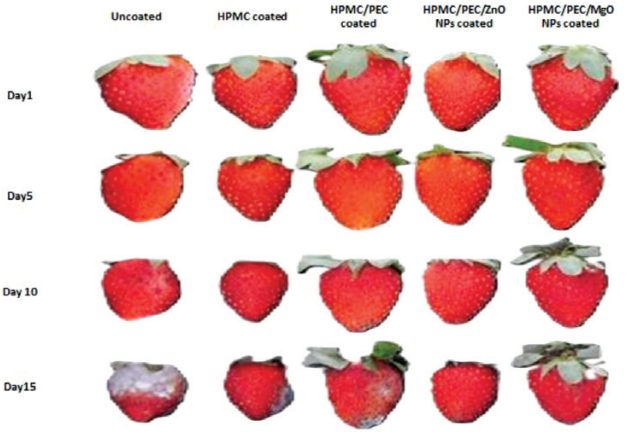

Figure 9: Visual changes in the strawberries over the storage period, showing the effects of different coatings

Table 2: Antimicrobial effects on coated and uncoated strawberries (diameter of zone of inhibition (mm))

Pathogenic bacterial strains	Uncoated	HPMC	HPMC/PEC	HPMC/PEC/ZnO	HPMC/PEC/MgO
Staphylococcus aureus (SA)	0	1.1 ± 0.4	1.9 ± 0.2	2.9 ± 0.1	3.1 ± 0.4
Bacillus cereus (BC)	0	1.5 ± 0.3	2.1 ± 0.4	2.7 ± 0.4	3.3 ± 0.6
Escherichia coli (E. coli)	0	1.8 ± 0.6	2.2 ± 0.5	3.1 ± 0.2	3.6 ± 0.3

crobial activity due to the protective qualities of the MgO coating. Moreover, titratable acidity declined in all samples, which is what typically happens during fruit respiration. However, as indicated in **Figure 8c**, the strawberries with the HPMC/PEC/MgO coating had the highest titratable acidity (8.98 on day 15), whereas the ZnO-based coating was the least effective, showing only 8.50. This further underscores the effectiveness of the MgO formulation in maintaining the freshness of strawberries. Overall, this research reveals that the HPMC/PEC/MgO coating is the most effective in preserving the quality of strawberries, reducing weight loss, stabilizing pH, and retaining acidity. These results indicate that the biocomposite film based on HPMC and pectin with MgO nanoparticles improves both physical and antimicrobial protection, which could potentially prolong the shelf-life of strawberries in postharvest storage.

6.2 Microbiological properties

Figure 9 includes the visual analysis of strawberries treated with various coatings (HPMC, HPMC/PEC, HPMC/PEC/ZnO, and HPMC/PEC/MgO) during a 10-day storage period, showing notable differences in their preservation effectiveness. On the first day, all strawberries looked fresh and undamaged, exhibiting no spoilage signs regardless of the coating type. However, by the tenth day, the strawberry without any coating displayed substantial deterioration, shrinkage, and microbial spoilage, highlighting its lack of preservation. The strawberry coated with HPMC/PEC showed a moderate level of dehydration and exhibited a dull surface, whereas the one coated solely with HPMC presented a similar outcome, but the coating was slightly less effective. The coating of HPMC/PEC/ZnO was more successful, as it maintained color and firmness with reduced visual damage, likely due to ZnO's antibacterial and antioxidant features. Importantly, the strawberry coated with HPMC/PEC/MgO demonstrated the best overall appearance, with minimal dehydration and no visible microbial growth, indicating its superior level of protection. This implies that incorporating MgO nanoparticles into the biopolymer matrix greatly improves the coating's barrier and antibacterial capabilities, making it the most efficient formulation among those evaluated.

Table 2 presents the antibacterial activity of coated and uncoated strawberries against *Bacillus cereus*, *Staphylococcus aureus*, and *Escherichia coli* after 10 d of storage. Five conditions were evaluated: uncoated (control group), HPMC-coated, HPMC/PEC-, HPMC/PEC/ZnO-, and HPMC/PEC/MgO-coated. The uncoated samples showed no inhibition (0 mm), confirming the absence of antibacterial activity. HPMC-coated samples exhibited very weak inhibition zones (1.1–1.8 mm), indicating a limited intrinsic antibacterial effect. The incorporation of pectin slightly enhanced this activity, with inhibition zones increasing to 1.9–2.2 mm, suggesting a minor synergistic interaction between HPMC and PEC. A more pronounced antibacterial effect was observed upon the addition of metal oxide nanoparticles. The HPMC/PEC/ZnO film exhibited moderate inhibition (2.7–3.1 mm), while HPMC/PEC/MgO showed the highest activity (3.1–3.6 mm), particularly against *E. coli*. This progressive increase in inhibition zones demonstrates that the antibacterial performance is mainly governed by the presence of nanoparticles, whereas the polymer matrix primarily acts as a carrier. The relatively small inhibition zones can be attributed to a limited diffusion of nanoparticles within the film matrix.

The results suggest that, to a certain extent, incorporation of MgO and ZnO nanoparticles into HPMC/PEC films markedly enhances their antibacterial performance, with MgO exhibiting the most pronounced effect, particularly against E. coli. The enhanced activity is primarily attributed to the generation of reactive oxygen species (ROS) and subsequent disruption of bacterial membranes.[28,29] These findings underscore the potential of MgO-based biopolymer coatings as effective antimicrobial agents in food packaging and biomedical applications, providing a strategy to inhibit microbial growth while maintaining the biocompatibility and barrier properties of the polymer matrix.

7 CONCLUSIONS

Biopolymer composite films for the preservation of *Fragaria vesca* (strawberries) were studied. The films were made of hydroxypropyl methylcellulose (HPMC) and pectin and were reinforced with magnesium oxide (MgO) and zinc oxide (ZnO) nanoparticles. Mechanical, rheological, structural, physicochemical and microbiological properties of the films were studied. The mechanical and rheological evaluations revealed that the addition of nanoparticles improved the films' flexibility and structural integrity, both of which are crucial for durability and handling during food storage. In addition, FTIR spectroscopy and SEM analysis verified that the polymers and nanoparticles interacted successfully while maintaining the biopolymer matrix's molecular stability. From a physicochemical standpoint, the films demonstrated encouraging biodegradation behavior, supporting

their environmentally friendly characteristics. The water vapor permeability (WVP) was acceptable, providing essential moisture barrier qualities for fruit preservation. In conclusion, the HPMC/pectin-based biocomposite films incorporating ZnO and MgO nanoparticles, exhibited a robust synergy of mechanical performance, antimicrobial activity, and environmental suitability. These results highlight the usefulness of employing such films as environmentally friendly substitutes for conventional plastic packaging. Industrial scalability, real-life storage life investigations, and the inclusion of other bioactive chemicals to further improve their usefulness could be the subjects of future research.

Author Contributions statement

Nour-Djihane Mazouzi: performed the experimental work, collected and analyzed the data, interpreted the results, and drafted the manuscript, contributed to the analysis and interpretation of the data. Khalida Boutemak: conception and design of the study, revised the manuscript critically for important intellectual content. Ahmad Haddad: contributed to the analysis and interpretation of the data. All authors have read and approved the final version of the manuscript and agree to be accountable for all aspects of the work, ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved.

Competing Interests

The authors declare that there are no competing interests.

Funding

No funding was received for this work.

Data availability

Data presented in this study are available on request from the corresponding authors.

Clinical trial number: not applicable.

Acknowledgments

We sincerely thank the Research Centre for Industrial Technologies (CRTI), EChahid Mohammed ABASSI (Algiers, Algeria), the Microbiology Laboratory of the Science and Nature Faculty, University of Chadhli ben Djedid El Taref, and the Laboratory of Functional Analysis of Chemical Engineering Department of the Process Engineering Faculty, the Science and Technology University of Saad Dahlab Blida 1 for providing funding for this research.

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