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DEVELOPMENT AND CHARACTERIZATION OF POLY(VINYL ALCOHOL)/SILVER NANOPARTICLE ACTIVE PACKAGING FILMS FOR STRAWBERRY PRESERVATION

BY

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Abstract. Poly(vinyl alcohol) (PVA) films incorporated with green-synthesized silver nanoparticles (AgNPs) using broccoli extract were developed as potential active packaging for strawberry preservation. AgNP formation was confirmed by a UV-Vis absorption peak at 419 nm with an absorbance of 1.4927, corresponding to localized surface plasmon resonance. Particle size analysis showed an average diameter of 44.88 ± 6.51 nm and a polydispersity index of 0.08 ± 0.03, indicating a relatively uniform dispersion. The films were evaluated for total phenolic content, DPPH activity, mechanical properties, and visual preservation performance. The 5 mL AgNP film without citric acid showed the highest phenolic content (1.40 mg GAE/g) and tensile strength (44.79 N/mm^2). However, DPPH results were unreliable because most inhibition values were negative. Strawberry application showed preliminary preservation potential, especially for 2.5 mL AgNP with citric acid, by reducing fungal growth and maintaining fruit appearance during storage, although moisture control requires further optimization.

Keywords: active packaging, PVA, silver nanoparticles, broccoli extract, strawberry preservation.

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1. Introduction

The accumulation of plastic waste has become a major global environmental concern, particularly in the food packaging sector, which contributes substantially to the use of synthetic polymer-based materials. Conventional plastics such as polyethylene and polystyrene offer advantages in terms of functionality, processability, and low production cost. However, their resistance to natural degradation and potential chemical migration into food systems have raised concerns regarding environmental sustainability and food safety (Gerassimidou *et al*., 2023; Groh *et al*., 2019). Therefore, the development of functional packaging based on biodegradable polymers and nanotechnology has become an important strategy for improving the sustainability of modern food packaging systems.

Poly(vinyl alcohol) (PVA) is a water-soluble synthetic polymer with promising potential as a matrix for biodegradable and active packaging films. PVA has several advantages, including good film-forming ability, optical transparency, flexibility, mechanical strength, and compatibility with food-related applications (Fan *et al*., 2025; Oun *et al*., 2022). However, neat PVA films still require functional modification to improve their antimicrobial activity and ability to extend the shelf life of fresh food products (Nwabor *et al*., 2020). One promising approach is the incorporation of bioactive nanomaterials, particularly silver nanoparticles (AgNPs), into the PVA matrix.

Silver nanoparticles are widely recognized as effective antimicrobial agents against various pathogenic microorganisms, including Gram-positive and Gram-negative bacteria. Their antimicrobial mechanism is commonly associated with the release of Ag^+ ions, interaction with microbial cell walls, penetration into the cytoplasm, disruption of enzymatic systems, and damage to proteins and genetic material, ultimately inhibiting microbial growth and causing cell death (More *et al*., 2023; Yin *et al*., 2020). Due to their nanoscale size, generally within the range of 1–100 nm, AgNPs possess a large specific surface area, allowing more effective interaction with microbial cells compared with bulk silver (Qing *et al*., 2018; Wypij *et al*., 2018).

Nevertheless, conventional chemical synthesis of AgNPs often involves toxic reducing agents such as sodium borohydride or other hazardous organic compounds, which may generate harmful residues (Xu *et al*., 2020; Zhang *et al*., 2016). To address this issue, green synthesis has emerged as a safer and more sustainable alternative. In this method, plant extracts are used as natural reducing and stabilizing agents (Eker *et al*., 2025; Villagrán *et al*., 2024). Broccoli (*Brassica oleracea* L.) contains phytochemical compounds such as flavonoids, glucosinolates, phenolic compounds, and other antioxidants that may reduce Ag^+ ions to Ag^0 and stabilize the resulting nanoparticles (Abdulazeem *et al*., 2023; Eker *et al*., 2025). This approach offers a more environmentally friendly synthesis route while potentially producing stable and bioactive AgNPs suitable for food packaging applications.

Strawberry (*Fragaria x Ananassa*) is a highly perishable fruit due to its high moisture content, soft texture, rapid postharvest respiration, and susceptibility to fungal spoilage (Contigiani *et al*., 2018). Quality deterioration in strawberries commonly involves color changes, tissue softening, water loss, microbial contamination, and fungal growth, particularly by *Botrytis cinerea* (Petrasch *et al*., 2019; Petrasch *et al*., 2022). Therefore, active packaging with antimicrobial properties is needed to help maintain strawberry quality and extend its shelf life.

Although PVA/AgNP films are promising as active packaging materials, their application requires comprehensive characterization. Mechanical testing is needed to evaluate tensile strength, elongation at break, and film durability. Total phenolic content analysis provides information on the potential contribution of plant-derived reducing agents remaining in the film. Antioxidant activity testing may indicate radical scavenging capacity, although method selection should be appropriate for polymeric films. In addition, application testing on strawberries is necessary to evaluate the practical preservation performance of the film under storage conditions. This study aimed to characterize PVA packaging films modified with green-synthesized silver nanoparticles using broccoli extract and to evaluate their potential application for strawberry preservation. The study focused on AgNP characterization, total phenolic content, DPPH antioxidant activity, mechanical properties, and visual observation of strawberry quality during storage.

2. Materials and Methods

2.1. Materials

The materials used in this study included PVA Poly(vinyl alcohol) (PVA; Mw 146,000−186,000 g/mol, 98% hydrolyzed), methanol, Folin-Ciocalteu reagent, sodium carbonate (Na_2CO_3), gallic acid, silver nitrate ($AgNO_3$), citric acid, and sulfuric acid. All reagents were purchased from Sigma-Aldrich. Fresh strawberries and broccoli samples for extract preparation were obtained from a local market in Bogor, West Java, Indonesia.

2.2. Preparation of Broccoli Extract

Fresh broccoli was washed, cut into small pieces, and blended with 100 mL distilled water until homogeneous. The mixture was heated in a water bath at 80°C for 15 min and filtered using Whatman No. 42 filter paper. The filtrate was stored in a dark bottle prior to use.

2.3. Green Synthesis of Silver Nanoparticles

Silver nanoparticles were synthesized by adding 5 mL broccoli extract to 95 mL of 1 mM $AgNO_3$ solution. The mixture was stirred at 60°C for 1 h until the color changed to reddish brown, indicating the formation of AgNPs. The resulting AgNP solution was referred to as solution A. The formation of AgNPs was confirmed using Analytik Jena SPECORD 250 Plus UV-Vis spectroscopy in the wavelength range of 400–700 nm.

2.4. Preparation of PVA/AgNP Composite Films

PVA powder (1 g) was dissolved in 25 mL distilled water and homogenized using a magnetic stirrer at 90°C. The AgNP solution was added into the PVA solution at different volumes, namely 2.5, 5, and 10 mL. The mixture was stirred briefly and sonicated for 30 min. Citric acid (0.375 g) was added as a crosslinking agent in selected formulations followed by the addition of 1 mL of 98%sulfuric acid as catalyst. The mixture was stirred at 70°C for 2 h, poured into molds, and dried in an oven at 50°C for 48 h. Films without citric acid were also prepared for comparison.

2.5. Characterization

The green-synthesized AgNPs were characterized using Analytik Jena SPECORD 250 Plus UV-Vis spectroscopy to identify the localized surface plasmon resonance peak. Particle size and polydispersity index were determined using PSA Nanotrac Wave II. Film samples were cut into rectangular strips of 2 × 7 cm. Tensile testing was performed using a Universal Testing Machine Testometric x350 5 kN at a crosshead speed of 2 mm/min. The tensile strength, elongation at break, strain, and Young's modulus were recorded to evaluate the mechanical performance of the films.

2.6. Total Phenolic Content

A 10 mg film sample was placed in 100 mL distilled water and stirred to obtain an aqueous extract of soluble and releasable film components. Then, 1 mL of the film extract solution was mixed with 1 mL Folin-Ciocalteu reagent. After 5 min, 2.5 mL of 5% Na_2CO_3 solution was added, and the mixture was diluted with distilled water to a final volume of 10 mL. The solution was homogenized and incubated in the dark for 1 h. Absorbance was measured at 725 nm using a UV-Vis spectrophotometer. Total phenolic content was calculated using a gallic acid calibration curve and expressed as mg gallic acid equivalent per gram sample (mg GAE/g).

2.7. DPPH Radical Scavenging Activity

The maximum wavelength of DPPH was determined by scanning a 0.2 mM DPPH solution in the range of 400–800 nm. For blank measurement, 2 mL DPPH solution was diluted with methanol to 5 mL and incubated for 30 min in the dark at room temperature. The absorbance was then measured at 517 nm. For sample testing, 2 g PVA/AgNP film was placed in 100 mL distilled water and stirred to obtain an aqueous extract/suspension with a nominal film concentration of 20,000 mg/L. The stock solution was diluted to concentrations of 4.000, 8.000, 12.000, 16.000, and 20.000 mg/L. Then, 1 mL of each sample solution was mixed with 2 mL DPPH solution and diluted with methanol to 5 mL. The mixture was incubated for 30 min in the dark at room temperature, and the absorbance was measured at 517 nm. The IC_{50} value was estimated from the linear regression equation.

2.8. Application of PVA/AgNP Films to Strawberries

Fresh strawberries were wrapped using PVA/AgNP films and stored for 5 days under controlled environmental conditions. Visual observations of color, texture, fungal growth, and spoilage were conducted daily.

3. Results and Discussion

Figure 1 presents the UV-Vis absorption spectrum of the AgNP solution synthesized using broccoli extract as a natural reducing and stabilizing agent. The UV-Vis spectrum of the AgNP solution synthesized using broccoli extract showed a maximum absorption peak at 419 nm. This absorption maximum falls within the typical surface plasmon resonance region of AgNPs, which is generally observed around 400–500 nm. The presence of this band confirms the formation of AgNPs and suggests the reduction of Ag^+ ions to metallic Ag^0 by phytochemicals present in the broccoli extract. In addition, the formation of a reddish-brown color during synthesis visually supported the formation of AgNPs, as this color change is commonly associated with the excitation of surface plasmon resonance in silver nanoparticles. Similar findings were reported by Abdulazeem *et al*. (2023), who synthesized AgNPs using aqueous broccoli floret extract and observed a color change from transparent to reddish-brown, followed by confirmation using UV-Vis spectroscopy. Other plant-mediated AgNP studies have also reported that the appearance of brown or reddish-brown color, together with a characteristic UV-Vis absorption band in the visible region, indicates successful AgNP formation (Rana *et al*., 2024; Subhani *et al*., 2024).

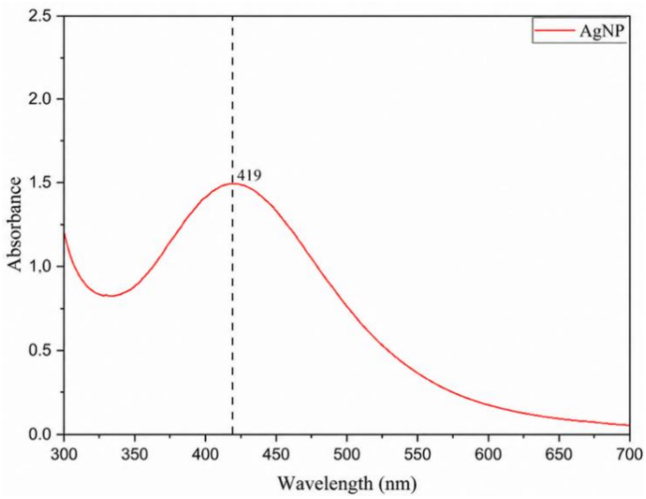


Fig. 1 – The UV-Vis absorption spectrum of the AgNP solution synthesized using broccoli extract.

The absorption peak observed at 419 nm suggests that the synthesized AgNPs were relatively large but still within the nanoscale range. A red shift of the AgNP surface plasmon resonance peak toward longer wavelengths is commonly associated with increased particle size, particle–particle interaction, or changes in the surrounding medium (Amendola *et al*., 2010; Leonov *et al*., 2023; Yeshchenko *et al*., 2012). This interpretation is supported by PSA results, which showed an average particle size of 44.88 ± 6.51 nm. The low polydispersity index of 0.08 ± 0.03 indicates a narrow particle size distribution and suggests that the AgNP suspension was relatively monodisperse and colloidally stable (Danaei *et al*., 2018). In addition, bioactive compounds in broccoli extract, such as flavonoids, phenolic acids, glucosinolates, and other antioxidant constituents, likely contributed to the reduction of Ag^+ to Ag^0 and stabilization of the formed AgNPs, as reported for broccoli-mediated and plant-mediated AgNP synthesis (Abdulazeem *et al*., 2023; Eker *et al*., 2025).

The total phenolic content of the PVA/AgNP films was determined using the Folin-Ciocalteu method. This method is based on an electron-transfer reaction in which phenolic compounds reduce phosphomolybdic-phosphotungstic complexes in the Folin-Ciocalteu reagent, producing a blue-colored complex that can be measured spectrophotometrically. Higher absorbance generally indicates a greater reducing response, which is commonly expressed as total phenolic content. However, the Folin-Ciocalteu assay is not completely specific to phenolic compounds because different phenolic structures and other reducing substances can also influence the assay response. Therefore, the obtained values should be interpreted cautiously as total phenolic content or total reducing capacity rather than as an exclusive measurement of phenolic compounds (Platzer *et al*., 2021; Raposo *et al*., 2024).

The total phenolic content of the PVA/AgNP films prepared with different AgNP volumes and citric acid treatments is presented in Table 1. The total phenolic content of the PVA/AgNP films varied depending on the volume of AgNP solution and the presence of citric acid. In the present study, the highest total phenolic content was observed in the film containing 5 mL AgNPs without citric acid, with a value of 1.40 mg GAE/g. Films containing 5 mL AgNPs with citric acid also showed relatively higher phenolic values compared with other citric acid-containing formulations. In contrast, some formulations showed negative calculated phenolic values, these values should not be interpreted as negative phenolic content; instead, they indicate that the absorbance response was below the quantifiable range of the method under the applied conditions and may have been affected by matrix background or spectral interference. This result highlights the importance of method validation because the Folin-Ciocalteu assay can be affected by matrix composition, reagent concentration, reaction time, wavelength selection, and calibration conditions (Raposo *et al*., 2024).

The results suggest that 5 mL AgNPs may represent an optimum concentration for maintaining or releasing phenolic-related reducing compounds in the film matrix. A higher AgNP volume did not result in higher total phenolic content, possibly due to nanoparticle aggregation, reduced availability of phenolic compounds, or stronger interactions between AgNPs and the polymer matrix. Similar studies on plant-mediated AgNP synthesis have shown that phenolic compounds, flavonoids, terpenoids, and other phytochemicals in plant extracts can act as reducing and stabilizing agents during AgNP formation, and their availability can influence nanoparticle formation, stability, and functional properties (Eker *et al*., 2025; Fahim *et al*., 2024).

Table 1
Total phenolic content of PVA/AgNP films

Film formulation	**Absorbance**	**Total phenolic content (mg GAE/g)**
2.5 mL AgNP + citric acid	0.0055	*BQL
10 mL AgNP + citric acid	0.0128	0.30
5 mL AgNP + citric acid	0.0176	0.81
2.5 mL AgNP	0.0083	*BQL
10 mL AgNP	0.0111	0.12
5 mL AgNP	0.0233	1.40

**BQL = below the quantifiable range of the Folin-Ciocalteu assay under the applied conditions. The original regression produced negative calculated values (-0.48 and -0.18 mg GAE/g), which were not interpreted as negative phenolic contents.*

The presence of citric acid appeared to reduce the measured phenolic content compared with films without citric acid. This reduction may be associated with the crosslinking effect of citric acid, which can form ester linkages between its carboxyl groups and hydroxyl groups in PVA, producing a more compact and stable polymer network. A denser matrix may restrict the release of phenolic-related compounds into the test solution, thereby lowering the amount of reducing compounds available to react with the Folin-Ciocalteu reagent. This interpretation is supported by recent studies showing that citric acid can act as an eco-friendly crosslinker in biopolymeric materials and can improve network stability through covalent interactions with hydroxyl-containing polymers (Dudeja *et al*., 2023; Huang *et al*., 2023). Therefore, although the Folin-Ciocalteu result suggests the presence of reducing compounds in the films, further analysis using more selective methods, such as HPLC-based phenolic profiling, ABTS assay, FRAP (Ferric Reducing Antioxidant Power) assay, or release-based antioxidant testing, is recommended to confirm the specific contribution of phenolic compounds in the PVA/AgNP films.

The antioxidant activity of the PVA/AgNP films was evaluated using the DPPH radical scavenging assay. DPPH is a stable free radical that exhibits a purple color and is commonly measured at 517 nm. In the presence of antioxidant compounds, DPPH radicals are reduced, resulting in a decrease in absorbance. Therefore, a lower absorbance value generally indicates stronger radical scavenging activity. However, the DPPH assay is highly sensitive to experimental conditions, including solvent compatibility, sample color, turbidity, reaction time, and possible spectral interference. These factors are particularly important for polymeric films and nanoparticle-containing systems, where active compounds may not be fully released into the reaction medium. The antioxidant activity results of the PVA/AgNP packaging films, evaluated using the DPPH method, are presented in Table 2.

Based on Table 2, most PVA/AgNP film formulations showed negative DPPH inhibition values, indicating that the absorbance of the sample-DPPH mixture was higher than that of the blank. For the film containing 2.5 mL AgNPs with 0.375 g citric acid, the inhibition values ranged from -15.00% at 4,000 mg/L to -275.29% at 16,000 mg/L, with a calculated IC_{50} value of -3503.24. The film containing 10 mL AgNPs with citric acid also showed negative inhibition values from -89.67% to -237.21%, with an IC_{50} value of -13.590. Similarly, the film containing 2.5 mL AgNPs without citric acid showed inhibition values ranging from -72.54% to -255.79%, while the films containing 10 mL and 5 mL AgNPs without citric acid showed highly negative inhibition values, reaching -315.92% and -293.25%, respectively. These negative inhibition values indicate that the DPPH assay did not produce a valid radical scavenging response for most film formulations.

Table 2
DPPH Antioxidant Activity of PVA/AgNP Packaging Films Synthesized Using Broccoli Extract

Film formulation	Concentration (mg/L)	Absorbance at 517 nm	DPPH inhibition (%)	Calculated IC_{50}
AgNP 2.5 mL + citric acid	4.000	0.5910	-15.00	-3503.24
	8.000	1.1276	-119.42	
	12.000	1.1093	-115.86	
	16.000	1.9286	-275.29	
	20.000	1.8829	-266.39	
AgNP 10 mL + citric acid	4.000	0.9747	-89.67	-13.590
	8.000	1.2205	-137.50	
	12.000	1.5825	-207.94	
	16.000	1.4880	-189.55	
	20.000	1.7329	-237.21	
AgNP 5 mL + citric acid	4.000	0.3607	29.81	-189.20
	8.000	0.8168	-58.94	
	12.000	1.2768	-148.45	
	16.000	1.7495	-240.44	
	20.000	1.0310	-100.62	
AgNP 2.5 mL	4.000	0.8867	-72.54	-25535.59
	8.000	1.3046	-153.86	
	12.000	1.7289	-236.43	
	16.000	1.8284	-255.79	
	20.000	1.2335	-140.03	
AgNP 10 mL	4.000	0.8311	-61.72	-6222.52
	8.000	1.5585	-203.27	
	12.000	1.7786	-246.10	
	16.000	2.0508	-299.07	
	20.000	2.1374	-315.92	
AgNP 5 mL	4.000	0.9200	-79.02	-858.74
	8,000	1.2923	-151.47	
	12.000	1.4919	-190.31	
	16.000	1.5382	-199.32	
	20.000	2.0209	-293.25	

Among all tested formulations, the only positive inhibition value was observed in the film containing 5 mL AgNPs with 0.375 g citric acid at 4 mg/L, which showed 29.81% inhibition. However, the inhibition values became negative at higher concentrations, namely -58.94%, -148.45%, -240.44%, and -100.62% at 8, 12, 16 and 20 mg/L, respectively. Another 5 mL AgNPs with citric acid formulation also showed negative inhibition values from -28.37% to -288.48%, with a calculated IC_{50} value of -12.2463. Therefore, although one formulation showed limited radical scavenging activity at the lowest concentration, the overall DPPH results were inconsistent and did not allow reliable IC_{50} determination.

The negative IC_{50} values should not be interpreted as true antioxidant inactivity or pro-oxidant behavior of the films. Instead, they indicate that the DPPH assay was not suitable for this PVA/AgNP film system under the applied experimental conditions. Several factors may explain these results. First, the active compounds derived from broccoli extract may have been trapped within the PVA matrix and were not completely released into the reaction solution. Second, incomplete film dissolution or extraction, particularly in the citric-acid-crosslinked films, may have limited the contact between antioxidant compounds and DPPH radicals. Third, AgNPs and film-derived components may have caused turbidity, light scattering, sample color interference, or baseline shifts, resulting in increased absorbance at 517 nm. Similar methodological concerns have been reported in recent studies, where DPPH analysis was shown to be affected by reaction conditions, spectroscopic interference, sample color, and inconsistencies in IC_{50} calculation (Celiz *et al*., 2020; De Menezes *et al*., 2021; Rumpf *et al*., 2023).

These findings suggest that DPPH may not be the most appropriate method for directly evaluating antioxidant activity in solid polymeric films or nanoparticle-containing packaging materials. For active packaging films, the antioxidant response depends not only on the presence of active compounds but also on their release from the polymer matrix into the food or test medium. Therefore, alternative or complementary assays such as ABTS, FRAP, Folin-Ciocalteu, and release-based antioxidant testing are recommended. ABTS and FRAP may provide more reproducible or complementary information because they involve different reaction mechanisms and may be less affected by some limitations observed in DPPH-based measurements (Rumpf *et al*., 2023; Santos *et al*., 2024). For future analysis, the film extract should be properly prepared, centrifuged or filtered before measurement, and corrected using a sample blank to minimize turbidity and color interference.

The mechanical properties of the PVA/AgNP films were evaluated to determine the effect of AgNP incorporation and citric acid addition on the strength, stiffness, and flexibility of the films. The tested parameters included stress at peak, strain at peak, strain at break, and Young's modulus, as presented in Table 3. These properties are important for food packaging applications because packaging films must have sufficient tensile strength to protect food products while maintaining adequate flexibility for handling and wrapping. The mechanical performance of PVA-based films can be modified by incorporating nanofillers such as AgNPs or by introducing crosslinking agents that alter the polymer network structure (Ali *et al*., 2024; Madivoli *et al*., 2022; Nguyen *et al*., 2024).

The neat PVA film showed a stress at peak of 27.50 N/mm^2, strain at peak of 10.76%, strain at break of 16.34%, and Young's modulus of 3694.83

N/mm^2. The incorporation of AgNPs without citric acid generally increased the tensile strength of the films. The film containing 2.5 mL AgNPs showed a slightly higher stress at peak of 29.69 N/mm^2 and a higher strain at break of 25.08%, indicating improved flexibility compared with neat PVA. Increasing the AgNP volume to 5 mL produced the highest stress at peak, 44.79 N/mm^2, and the highest Young's modulus, 6705.30 N/mm^2. This result indicates that the 5 mL AgNP formulation had the strongest and stiffest film structure. The improvement may be associated with the reinforcing effect of AgNPs within the PVA matrix, where well-dispersed nanoparticles can restrict polymer chain mobility, promote interfacial interactions with hydroxyl-rich PVA chains and plant-extract-derived capping compounds, and enhance stress transfer within the film network. Similar improvements in PVA-based nanocomposite films have been reported by Madivoli *et al.* (2022), who showed that the incorporation of cellulose nanofibrils and AgNPs enhanced the mechanical and antimicrobial properties of PVA nanocomposite films. Nguyen *et al.* (2024) also reported that AgNP-containing PVA-based active films showed improved mechanical performance due to enhanced interactions between the polymer matrix and the incorporated nanofillers.

Table 3

Mechanical Properties of PVA/AgNP Films Determined by UTM Analysis

Film formulation	**Stress at peak (N/mm^2)**	**Strain at peak (%)**	**Strain at break (%)**	**Young's modulus (N/mm^2)**
PVA	27.50	10.76	16.34	3694.83
AgNP 2.5 mL + citric acid	16.00	11.92	21.25	1246.10
AgNP 10 mL + citric acid	35.52	11.08	23.07	4294.07
AgNP 5 mL + citric acid	19.61	12.68	21.83	1355.58
AgNP 2.5 mL	29.69	15.70	25.08	3049.82
AgNP 10 mL	40.81	1.78	34.69	4360.66
AgNP 5 mL	44.79	1.06	4.05	6705.30

However, the increase in strength was accompanied by a significant reduction in flexibility. The AgNP 5 mL film showed a strain at peak of only 1.06% and strain at break of 4.05%, indicating that the film became rigid and brittle. This stiffening behavior can be explained by the reduced mobility of PVA chains when AgNPs and phytochemical capping components interact with hydroxyl groups in the polymer network. At moderate loading, these interactions may improve stress transfer and tensile strength. At higher or non-uniform loading, however, AgNPs may form localized aggregates that act as rigid domains and stress concentration sites. These regions can initiate microcracks, reduce homogeneous deformation, and promote brittle failure. The AgNP 10 mL film also showed high stress at peak, 40.81 N/mm^2, and Young's modulus, 4360.66 N/mm^2. However, its strain at peak was only 1.78%, suggesting early maximum stress and limited elastic deformation before structural instability. Although the strain at break of the AgNP 10 mL film was recorded as 34.69%, this large discrepancy between strain at peak and strain at break should be interpreted cautiously because it may reflect UTM recording behavior, specimen slippage, partial tearing, or post-peak extension after microcracking rather than uniform plastic deformation. Since repeated UTM measurements for this batch were not available at the revision stage, this value is retained only as an observed anomalous result, and no definitive mechanistic conclusion is drawn from it. Repeated testing with replicate specimens is required to confirm the deformation behavior of the 10 mL AgNP film. A high AgNP content can potentially increase nanoparticle aggregation, creating stress concentration points and non-uniform regions within the polymer matrix. Such structural defects may reduce flexibility and make the film more prone to brittle failure. This interpretation is consistent with previous studies indicating that excessive or poorly dispersed nanofillers can reduce film homogeneity and negatively affect mechanical behavior, even when tensile strength increases (Madivoli *et al.*, 2022; Nguyen *et al.*, 2024).

Citric acid addition also changed the mechanical behavior of the PVA/AgNP films. The films containing citric acid generally showed lower Young's modulus values than the corresponding films without citric acid, except for the 10 mL AgNP + citric acid formulation. The AgNP 2.5 mL + citric acid film showed a stress at peak of 16.00 N/mm^2, strain at break of 21.25%, and Young's modulus of 1246.10 N/mm^2. The AgNP 5 mL + citric acid film had a stress at peak of 19.61 N/mm^2, strain at break of 21.83%, and Young's modulus of 1355.58 N/mm^2. These results indicate that citric acid-containing films were generally more flexible but less stiff than the AgNP 5 mL film without citric acid. Citric acid can act as a crosslinking agent by forming ester linkages between its carboxyl groups and the hydroxyl groups of PVA, thereby modifying the polymer network. Recent studies have reported that citric acid is an eco-friendly crosslinker for hydroxyl-containing biopolymers and can improve the stability, swelling resistance, and mechanical behavior of PVA-based films or membranes through esterification and network formation (Ali *et al.*, 2024; Dudeja *et al.*, 2023; Huang *et al.*, 2023).

Among the citric acid-containing films, the AgNP 10 mL + citric acid formulation showed the highest mechanical strength, with a stress at peak of 35.52 N/mm^2, strain at break of 23.07%, and Young's modulus of 4294.07 N/mm^2. This suggests that, in the presence of citric acid, a higher AgNP content may contribute to a more balanced mechanical performance by improving strength while maintaining moderate flexibility. In comparison, the AgNP 5 mL + citric acid film showed lower tensile strength but retained higher flexibility than the AgNP 5 mL film without citric acid. The improved flexibility of citric acid-containing films may be related to changes in the polymer network structure and intermolecular interactions induced by crosslinking, as also reported for citric-acid-crosslinked PVA-based materials (Ali *et al*., 2024; Huang *et al*., 2023).

Overall, the AgNP 5 mL film without citric acid showed the highest strength and stiffness, making it suitable for applications requiring stronger mechanical protection. However, its low strain at break indicates limited flexibility, which may be less suitable for wrapping fragile fruits such as strawberries. In contrast, citric acid-containing formulations, especially AgNP 10 mL + citric acid and AgNP 5 mL + citric acid, provided better flexibility and may be more appropriate for packaging applications requiring conformability. Therefore, the optimum formulation should be selected based on the intended packaging function: high-strength films may be suitable for mechanical protection, while more flexible films may be preferable for direct fruit wrapping.

The preservation performance of the PVA/AgNP films was evaluated by applying the films to fresh strawberries and observing visual quality changes during 5 days of storage. Figure 2 showed visual appearance of strawberries packaged with PVA/AgNP films during 5 days of storage The observed parameters included color retention, browning, softening, visible fungal growth, and overall spoilage development. As shown in Figure 2, all strawberry samples underwent visible quality deterioration during storage, although the deterioration rate differed among treatments. The control sample (A0) gradually lost its fresh red appearance and showed severe darkening and visible fungal growth by day 5. This result is consistent with previous studies reporting that strawberries are highly perishable fruits with a short postharvest life and that their quality deterioration is commonly associated with color change, firmness loss, weight loss, microbial growth, and decay development (Pasha *et al*., 2023; Rasouli *et al*., 2025).

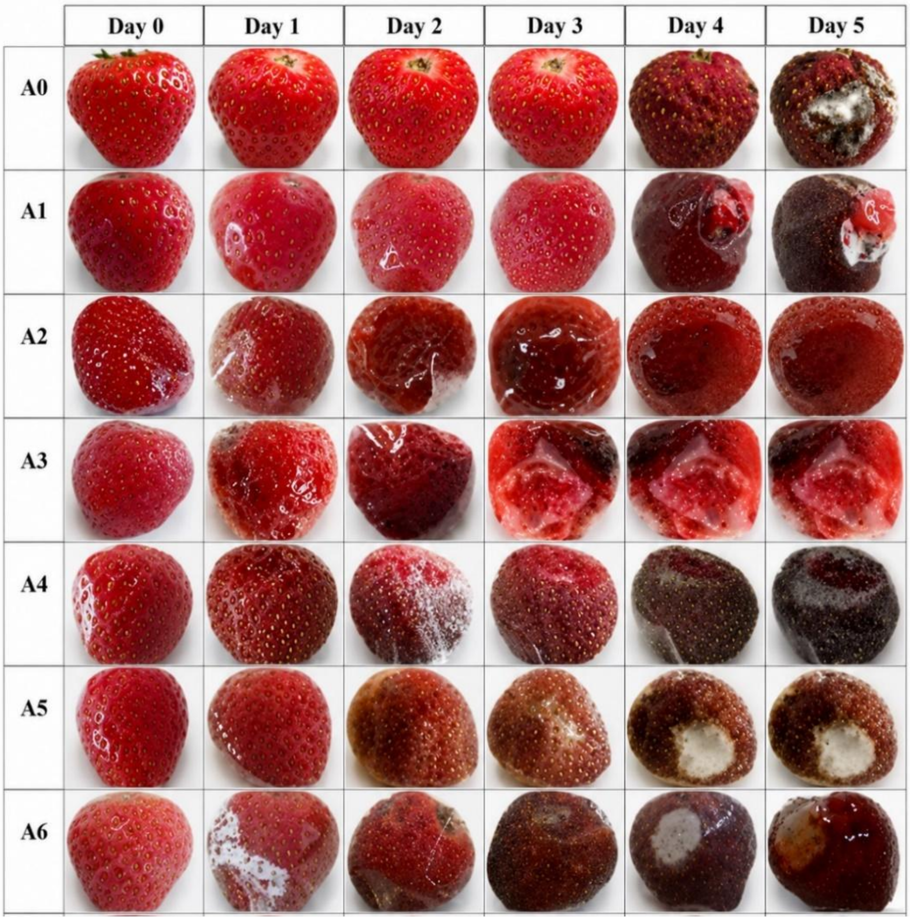
The samples wrapped with PVA/AgNP films showed different levels of preservation performance. Some packaged strawberries still developed fungal growth during storage, particularly in formulations that appeared to retain more moisture inside the package. This may be attributed to the closed packaging environment, where fruit respiration and water vapor retention increase the relative humidity around the fruit. High humidity and water activity can create a favorable microenvironment for fungal development. Rabasco-Vílchez *et al*. (2025) reported that B. cinerea is the primary fungus responsible for strawberry postharvest decay and that its germination is strongly affected by storage temperature and water activity. Therefore, although AgNPs possess antimicrobial properties, their effectiveness in strawberry packaging may be limited if excessive moisture accumulates inside the package.

The incorporation of AgNPs was expected to contribute to antimicrobial protection because silver nanoparticles can inhibit microbial growth through the release of Ag^+ ions, disruption of microbial cell membranes, oxidative stress generation, and interference with cellular components. Recent reviews have emphasized that AgNPs are promising antimicrobial additives in food packaging because they can reduce microbial contamination, delay spoilage, and help extend the shelf life of packaged foods (Okur *et al*., 2025). In the present study, however, the visual results indicate that antimicrobial activity alone was not sufficient to fully prevent fungal growth under humid storage conditions. This suggests that active packaging for strawberries should not only provide antimicrobial activity but also regulate water vapor transmission and internal package humidity.

Citric acid also influenced the visual preservation performance of the packaged strawberries. Samples containing citric acid, particularly A1, showed relatively better early-stage visual quality, with delayed fungal growth and better color retention compared with several formulations without citric acid. Citric acid may contribute to preservation through mild antimicrobial activity, local pH reduction, and modification of the PVA film network. As a crosslinking agent, citric acid can interact with hydroxyl-containing polymers such as PVA and improve film stability, homogeneity, and flexibility (Ali *et al*., 2024; Zhang *et al*., 2023). However, citric acid-containing films may also retain moisture depending on formulation, film hydrophilicity, and packaging conditions. Excessive moisture retention may accelerate softening or surface sliminess in strawberries, especially when the package is not sufficiently permeable to water vapor.

Among the tested formulations, A1 (AgNP 2.5 mL + citric acid) showed the most balanced visual performance. This sample maintained a relatively fresh red color until approximately day 3 and showed slower visual deterioration than several other treatments. Although fungal growth and darkening were still observed by day 5, the early-stage preservation performance suggests a possible synergistic effect between AgNP antimicrobial activity and citric-acid-mediated film modification. In contrast, A4, A5, and A6, which contained AgNPs without citric acid, showed more pronounced browning, softening, and visible fungal growth during storage.

Overall, the visual observation suggests that PVA/AgNP films have preliminary potential as active packaging for strawberries, but their effectiveness depends strongly on film formulation and moisture control. The results also indicate that excessive humidity inside the package may counteract the antimicrobial benefit of AgNPs. Therefore, further optimization should focus on balancing antimicrobial activity with water vapor permeability, humidity regulation, and film flexibility. Since the present strawberry application test was based mainly on visual observation, the preservation claim should be considered preliminary. Future studies should include quantitative measurements such as weight loss, firmness, color parameters, total viable count, yeast and mold count, respiration rate, water activity, relative humidity inside the package, and silver migration analysis to confirm the safety and effectiveness of PVA/AgNP films for strawberry preservation.



A0: control/blank; A1: AgNP 2.5 mL + citric acid; A2: AgNP 10 mL + citric acid; A3: AgNP 5 mL + citric acid; A4: AgNP 2.5 mL; A5: AgNP 10 mL; A6: AgNP 5 mL

Fig. 2 − Visual appearance of strawberries packaged with PVA/AgNP films during 5 days of storage.

4. Conclusion

PVA films incorporated with green-synthesized silver nanoparticles using broccoli extract were successfully developed and characterized as potential active packaging materials for strawberry preservation. The formation of AgNPs was confirmed by the presence of a UV-Vis absorption peak at 419 nm, while particle size analysis showed an average particle size of 44.88 ± 6.51 nm, indicating successful nanoparticle formation through the green synthesis approach. Among the tested formulations, the film containing 5 mL AgNPs without citric acid exhibited the highest total phenolic content and the highest mechanical strength, suggesting that this formulation provided an optimum AgNP concentration for improving the structural performance of the PVA film.

The DPPH assay did not provide reliable antioxidant activity results, as most formulations showed negative inhibition values and negative IC_{50} values. These results are more likely associated with the limitations of the DPPH method for solid polymeric film systems, including limited release of active compounds, incomplete film dissolution, turbidity, and possible spectral interference, rather than indicating the complete absence of antioxidant potential. Therefore, further antioxidant evaluation using more suitable methods, such as ABTS, FRAP, or release-based antioxidant assays, is recommended.

The application of PVA/AgNP films to strawberries showed preliminary preservation potential, particularly in formulations containing both AgNPs and citric acid. However, visual observation also indicated that excessive humidity inside the packaging could promote fungal growth and fruit softening in several treatments. These findings suggest that the effectiveness of PVA/AgNP films as active packaging depends not only on antimicrobial activity but also on moisture regulation and packaging design. Further optimization of film formulation, water vapor control, active compound release, and quantitative postharvest quality evaluation is required before the developed films can be recommended for practical strawberry preservation.

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DEZVOLTAREA ȘI CARACTERIZAREA FILMELOR DE AMBALARE ACTIVĂ PE BAZĂ ALCOOL POLIVINILIC/NANOPARTICULE DE ARGINT PENTRU CONSERVAREA CĂPŞUNILOR

(Rezumat)

Filmele de alcool polivinilic (PVA) cu nanoparticule de argint (AgNP) încorporate, obținute prin sinteză verde folosind extract de broccoli au fost dezvoltate ca potențiale materiale de ambalare activă pentru conservarea căpşunilor. Formarea nanoparticulelor de Ag a fost confirmată prin maximul de absorbție UV-Vis la 419 nm, cu o absorbție de 1,4927, corespunzătoare rezonanței plasmonilor de suprafață localizați. Analiza dimensiunii particulelor a indicat un diametru mediu de 44,88 ± 6,51 nm și indicele de polidispersitate de 0,08 ± 0,03, sugerând o dispersie relativ uniformă. Filmele au fost evaluate din punctul de vedere al conținutului total de compuși fenolici, activității DPPH, proprietăților mecanice și performanței vizuale în conservarea fructelor. Filmul cu 5 mL AgNP fără acid citric a prezentat cel mai ridicat conținut fenolic (1,40 mg GAE/g) și cea mai mare rezistență la tracțiune (44,79 N/mm^2). Totuși, rezultatele DPPH au fost nesigure, deoarece majoritatea valorilor de inhibiție au fost negative. Aplicarea pe căpşuni a arătat potențialul preliminar de conservare, în special pentru filmul cu 2,5 mL AgNP și acid citric, prin reducerea dezvoltării fungice și menținerea aspectului fructelor pe durata depozitării, deși controlul umidității necesită optimizare suplimentară.