

Cellulose Nanocrystals and Zinc Oxide in Pineapple Starch Films for Enhanced Banana Shelf-Life

(Nanokristal Selulosa dan Zink Oksida dalam Filem Kanji Nanas untuk Jangka Hayat Pisang yang Dipertingkatkan)

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ABSTRACT

This study investigates the development of biodegradable films from pineapple stem starch enhanced with cellulose nanocrystals (CNC) and zinc oxide (ZnO) nanoparticles for improved food preservation. The film-forming behavior of pineapple stem starch was examined with varying concentrations of glycerol (0-30%), CNC (0-1.5%), and ZnO (0-20%). Rheological measurements showed that glycerol concentrations significantly influenced the viscoelastic properties of the starch solutions, with a notable peak in viscosity observed at 20% glycerol. The addition of CNC increased the storage modulus (G') and viscosity of the starch solutions, indicating enhanced structural integrity. ZnO nanoparticles imparted effective UV-blocking capabilities to the films, with optimal performance observed at 10% concentration. Water vapor permeability (WVP) of the films slightly increased with ZnO content, ranging from 0.0127 to 0.0157 $\text{g}\cdot\text{m}^{-1}\cdot\text{h}^{-1}\cdot\text{Pa}^{-1}$. Scanning electron microscopy (SEM) analysis showed uniform dispersion of ZnO nanoparticles within the starch matrix. The ZnO-enhanced starch coatings effectively extended the shelf life of bananas by delaying the ripening process. This study demonstrates the potential of pineapple stem starch-based films enhanced with CNC and ZnO as a sustainable and effective solution for food packaging, contributing to reduced food waste and environmental impact.

Keywords: Biodegradable films; cellulose nanocrystals; food preservation; starch

ABSTRAK

Penyelidikan ini mengkaji pembangunan filem terbiodegradasi daripada kanji batang nanas yang dipertingkatkan dengan nanokristal selulosa (CNC) dan nanozarah zink oksida (ZnO) untuk pengawetan makanan yang lebih baik. Tingkah laku pembentukan filem kanji batang nanas dikaji dengan pelbagai kepekatan gliserol (0-30%), CNC (0-1.5%) dan ZnO (0-20%). Pengukuran reologi menunjukkan bahawa kepekatan gliserol mempengaruhi sifat viskoelastik larutan kanji secara signifikan dengan peningkatan ketara dalam kelikatan diperhatikan pada 20% gliserol. Penambahan CNC meningkatkan modulus penyimpanan (G') dan kelikatan larutan kanji, menunjukkan peningkatan integriti struktur. Nanozarah ZnO memberikan keupayaan menghalang UV yang berkesan kepada filem, dengan prestasi optimum diperhatikan pada kepekatan 10%. Kebolehtelapan wap air (WVP) filem sedikit meningkat dengan kandungan ZnO, berkisar antara 0.0127 hingga 0.0157 $\text{g}\cdot\text{m}^{-1}\cdot\text{j}^{-1}\cdot\text{Pa}^{-1}$. Analisis mikroskopi elektron imbasan (SEM) menunjukkan penyebaran seragam nanozarah ZnO dalam matriks kanji. Salutan kanji yang dipertingkatkan dengan ZnO berkesan memanjangkan jangka hayat pisang dengan melambatkan proses peranakan. Kajian ini menunjukkan potensi filem berasaskan kanji batang nanas yang dipertingkatkan dengan CNC dan ZnO sebagai penyelesaian yang lestari dan berkesan untuk pembungkusan makanan, menyumbang kepada pengurangan sisa makanan dan kesan alam sekitar.

Kata kunci: Filem terbiodegradasi; kanji; nanohablur selulosa; pengawetan makanan

INTRODUCTION

Plastic pollution is a significant environmental challenge globally (MacLeod et al. 2021). While the durability and wide application of plastic materials have made them ubiquitous in modern society, this same durability leads to the persistence of plastic waste, which is difficult to degrade and causes serious ecological and health problems (Law & Narayan 2021). In addition to macroscopic plastic pollution, microplastic pollution, characterized by plastic particles, fibers, or fragments smaller than 5 mm, is increasingly drawing attention (Amrutha & Warriar 2020; Kurniawan et al. 2021). These tiny particles can infiltrate the environment through various pathways, posing significant risks to ecosystems and human health (Yuan, Nag & Cummins 2022). Microplastics, often originating from the breakdown of larger plastic items, are present in diverse environments including oceans, freshwater bodies, and soil. These particles, frequently resulting from the degradation of larger plastic objects, can infiltrate food webs and may pose health risks to a wide range of living organisms (Tang et al. 2021).

Starch, a polysaccharide found in many plants, offers a promising alternative for developing environmentally friendly materials due to its biodegradability and abundance (Cheng et al. 2021; Safinta Nurindra, Afist Azkiya & Yanas Anggana 2023; Smith & Zeeman 2020; Ummi Habibah et al. 2022). Starch-based plastics, derived from renewable sources, such as corn, potatoes, and cassava, offer several environmental benefits, including reduced reliance on fossil fuels and lower carbon emissions during production (Onyeaka et al. 2022).

The use of starch-based plastics in packaging, particularly food packaging, is growing due to their biodegradability and renewability (Cheng et al. 2021). However, these materials generally have lower mechanical properties compared to traditional plastics, limiting their application in areas requiring high durability (Bangar et al. 2021). Additionally, large-scale production could raise concerns about competition with food resources (do Val Siqueira et al. 2021).

Pineapple stems, often discarded as waste, present an untapped resource for starch extraction (Vieira et al. 2022). This starch exhibits unique properties, such as high amylose content, making it suitable for various applications without significantly impacting food production (Sriprablom et al. 2023). Prior studies have shown that adding materials like glycerol, CNC, and ZnO can enhance the properties of starch-based films (Caicedo et al. 2022).

The objective of this study was to develop and characterize biodegradable films from pineapple stem starch, incorporating glycerol, cellulose nanocrystals (CNCs), and zinc oxide (ZnO) to enhance food preservation. The research focuses on optimizing the composition of these films by examining the effects of these additives on

the rheological behavior and gelatinization temperature of the starch solutions. By understanding the effect of glycerol, CNCs, and ZnO on the viscosity, viscoelastic properties, and thermal behavior of the starch matrix, this study aims to create a film with improved mechanical and functional properties suitable for extending the shelf life of bananas.

MATERIALS AND METHODS

MATERIALS

Pineapple stem starch powder was prepared from pineapple stem waste according to previous study (Bumrungnok et al. 2023). Analytical grade glycerol was supplied by Sigma-Aldrich (USA). Cellulose nanocrystal (CNC) was obtained from CelluForce (Canada). Zinc oxide powder (ZnO) was obtained from Merck.

METHODOLOGY

For the preparation of the pineapple stem starch mixture, 10 g of starch was dispersed in 100 mL of water to create a 10% (w/v) solution. Glycerol was then sequentially added at concentrations of 0%, 1%, 2%, and 3% (w/w) relative to the total biopolymer content, ensuring thorough mixing for uniform plasticizer distribution. The mixture was gelatinized in domestic microwave oven (Panasonic NN-SM330M model) at medium heat, with intermittent stirring every 30 s using a glass rod for a total of six intervals to ensure adequate gelatinization.

To prepare the base solution, 10 g of pineapple stem starch was added into 100 mL of water, followed by the addition of 2 g of glycerol to act as a plasticizer. Cellulose nanocrystals (CNC) were incrementally added in quantities of 0 g, 0.05 g, 0.1 g, and 0.15 g, with rigorous stirring after each addition to ensure homogeneity. The resulting mixture underwent gelatinization in the microwave oven at medium heat, with intermittent stirring every 30 s for six cycles to achieve a consistent texture.

For the CNC stock solution, 0.5 g of CNC was dispersed by sonication in 500 mL of water to ensure complete dispersion. A 100 mL aliquot of this solution was taken to which 2 g of glycerol and 10 g of pineapple stem starch were added, followed by stirring to achieve uniform distribution. Varying amounts of zinc oxide (ZnO) were then incorporated in increments of 0 g, 0.25 g, 0.5 g, 1 g, and 2 g, with thorough stirring after each addition to ensure proper dispersion.

The final mixture was gelatinized in the microwave oven at medium heat, involving intermittent stirring and removal every 30 s for six intervals to ensure even heating. After gelatinization, 10 g of the sample was carefully poured into a tray (10 × 10 cm²) and dried in an oven at 40 °C until the film was fully formed.

CHARACTERIZATIONS OF FILM-FORMING SOLUTION

RHEOLOGICAL MEASUREMENTS

Steady-state flow and dynamic viscoelasticity measurements of the nanocomposite film-forming solutions were conducted at 20 °C using a rotational rheometer equipped with concentric cylinder geometry. First, steady shear flow measurements were performed over a shear rate range of 0.01–100 s⁻¹, and flow curves were obtained. Subsequently, strain sweep measurements were conducted at a frequency of 1 Hz to determine the storage modulus (G') and loss modulus (G'') as a function of strain.

UV-Vis SPECTROSCOPY ANALYSIS OF FILMS

UV-Vis spectroscopy was performed on the bio-nanocomposite films using a spectrophotometer. Film samples were placed directly into the spectrophotometer test cell, with air serving as the reference. The optical absorbance and transmittance of the films were measured across a wavelength range of 200–800 nm.

SEM ANALYSIS

The surface morphology of the developed films was analyzed using scanning electron microscopy (SEM) (ZEISS SUPRA 55VP). SEM analysis was conducted under vacuum conditions with an accelerating voltage of 10 kV. To enhance imaging, a thin layer of gold was applied to the non-conductive film samples prior to analysis.

WATER VAPOR PERMEABILITY (WVP)

The water vapor transmission rate (WVTR) and water vapor permeability (WVP) were calculated using the following equations:

$$\text{WVTR (g} \cdot \text{m}^{-2} \cdot \text{day}^{-1}) = G_t / A \quad (1)$$

where G_t is the rate of weight change over time, derived from the slope of the graph between time and weight change (g·day⁻¹). A is the surface area of the sample (m²). For a film with a diameter of 6 cm, $A = 0.0283$ m².

$$\text{WVP (g} \cdot \text{m}^{-1} \cdot \text{h}^{-1} \cdot \text{Pa}^{-1}) = (\text{WVTR} \times \text{Thickness of the film}) / \Delta P \quad (2)$$

where ΔP is the pressure difference, calculated as follows:

$$\Delta P = P_s \times (\Delta RH / 100) \quad (3)$$

where ΔRH represents the difference between the internal humidity (%RH = 0) and the external humidity of the cup at the beginning (%RH = 75), so $\Delta RH = 75$. P_s is the vapor pressure of water at 25.5 °C, equals to 3.173 kPa.

SHELF-LIFE EXTENSION OF BANANAS COATED WITH PINEAPPLE STEM STARCH

The bananas were fully submerged in the freshly prepared starch film-forming solution, ensuring complete coverage of the surface. The entire submersion process, from the initial dip to the final pull-out, took approximately 5 s. After coating, the bananas were allowed to dry at room temperature. The condition of the coated bananas was monitored and recorded every 2 days over a designated period. Photographs were taken using a camera at each interval to visually document changes in the bananas' appearance, including the progression of ripening and the development of any discoloration. This procedure allowed for a detailed analysis of the film's effectiveness in extending the bananas' shelf life and preserving their quality over time.

RESULTS AND DISCUSSION

EFFECT OF GLYCEROL CONCENTRATION ON THE RHEOLOGICAL BEHAVIOR OF STARCH

Rheological tests were performed at 20 °C to examine the flow behavior of the starch solution over a shear rate range from 0.01 to 100 s⁻¹. The results shown in Figure 1(a) demonstrated that the viscosity of the starch blends initially increased, reaching a peak before decreasing as the glycerol concentration increased. This reduction in viscosity can be attributed to glycerol which serves as a plasticizer, diminishing intermolecular interactions within the starch matrix, thereby reducing overall viscoelastic properties (Taghizadeh & Favis 2013).

At lower shear rates, a clear shear-thickening behavior was observed, where viscosity increased with increasing shear rate. However, at higher shear rates, a shear-thinning behavior was evident, where viscosity decreased as shear rate increased. This phenomenon may be related to the disentanglement and reorientation of polymer chains under high shear stress (Duan et al. 2024).

The viscosity measurements, as shown in Figure 1(b), showed a notable peak at all glycerol concentration, suggesting a complex interaction between the starch and glycerol at this specific ratio. The 20% glycerol showed the highest viscosity which may be due to the formation of a highly structured network at the molecular level that more effectively resist flow compared to other concentrations (Duan et al. 2024). This enhanced viscosity could be attributed to increased hydrogen bonding between the starch and glycerol molecules, leading to a more interconnected and rigid network structure. The high viscosity observed at 20% glycerol may also indicate an optimal balance between the plasticizing effect of glycerol and the cohesive properties of the starch, resulting in a more robust matrix. However, it is important to consider that excessive glycerol concentrations may disrupt this balance, leading to a decrease in viscosity as observed in the 30%

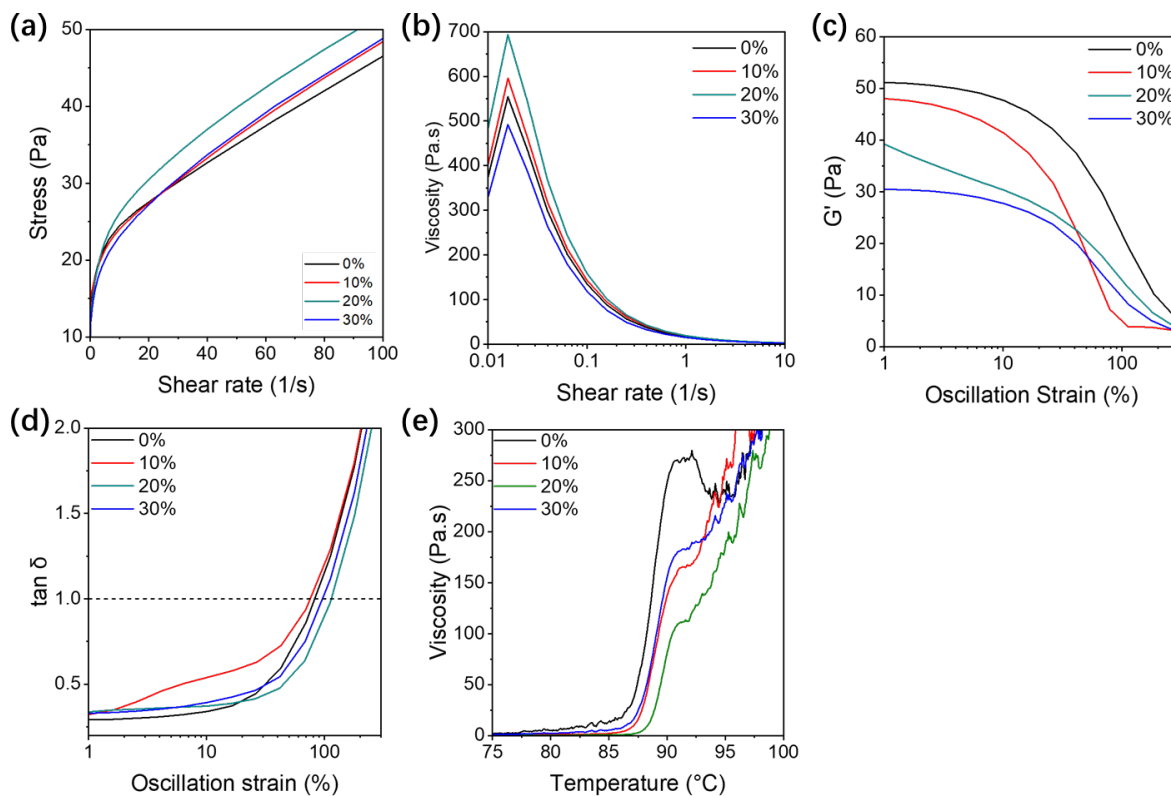


FIGURE 1. (a) Stress response of starch solutions with varying glycerol concentration as a function of angular velocity, (b) Viscosity profiles of starch solutions with varying glycerol concentrations as a function of angular velocity, (c) Storage modulus (G') of starch solutions with varying glycerol concentration, (d) $\tan \delta$ from oscillation tests of starch solutions with varying glycerol concentrations, and (e) Effect of varying glycerol concentration on the gelatinization temperature of starch solutions

glycerol solution. This could be due to an overabundance of glycerol molecules hindering the formation of strong intermolecular interactions within the starch network.

The viscosity measurements, as shown in Figure 1(b), showed a notable peak at all glycerol concentration, suggesting a complex interaction between the starch and glycerol at this specific ratio. The 20% glycerol showed the highest viscosity which may be due to the formation of a highly structured network at the molecular level that more effectively resist flow compared to other concentrations (Duan et al. 2024). The high viscosity observed at 20% glycerol may also indicate an optimal balance between the plasticizing effect of glycerol and the cohesive properties of the starch, resulting in a more robust and less deformable matrix (Zhang, Song & Zheng 2008). As the glycerol concentration deviates from this 20%, either by increasing or decreasing, the viscosity of the mixture decreases, demonstrating a clear dependence of the matrix's rheological properties on glycerol concentration. This behavior reveals the subtle link between polymer-plasticizer interactions and their macroscopic flow characteristics (Valencia, Henao & Zapata 2013).

In the rheological assessment of pineapple stem starch mixed with various glycerol concentrations, a significant peak in viscosity was observed at a 20% glycerol concentration, revealing shear-thinning behavior. This observation prompted further analysis using oscillatory rheological testing at 20 °C, a method commonly employed to evaluate the viscoelastic properties of biopolymer mixtures (Florjani, Zupani & Žumer 2002). The test results particularly the ratio of the loss modulus (G'') to the storage modulus (G'), expressed as $\tan \delta$, provided valuable insights into the material's behavior. The G' , indicative of the energy stored in the material and thus reflective of solid-like behavior, is influenced by the hardness of molecular chains, and the quantity of intermolecular bonds, much like the intramolecular associations observed in Halberd amylopectin (Tako & Hizukuri 2003). Conversely, the G'' measures the energy dissipated or lost (as heat) per cycle of sinusoidal deformation, indicating liquid or viscous behavior, which can be attributed to the movement and friction of molecules during testing. The $\tan \delta$, as a measure of the ratio of G'' to G' , is a critical parameter; a smaller $\tan \delta$ signifies a more pronounced gel-

like structure due to increased intermolecular interactions, or vice versa (Matalanis, Campanella & Hamaker 2009). This is consistent of the behavior observed in Halberd amylopectin, where the storage modulus was rather small and decreased with increasing temperature, suggesting a dominance of viscous behavior over elastic (Tako & Hizukuri 2003).

From Figure 1(c), it can be observed that all starch solutions exhibit an LVR, as evidenced by the relatively flat regions in the G' and G'' curves. The presence of glycerol, even at low concentrations, appears to expand the LVR, suggesting that the plasticizer is effective in reducing the resistance to deformation, thus, allowing for larger strains before the material's structure begins to break down (Muscat et al. 2012). This is particularly important for applications, such as food coatings or films, where the material may be subjected to mechanical stress during processing or use.

According to Figure 1(d), the $\tan \delta$ values for all glycerol concentrations initially decrease with increasing strain, indicating a transition from a more viscous to a more elastic behaviour. This suggests that at low strains, the starch molecules and glycerol plasticizer are able to reorganize themselves in response to deformation, storing more energy elastically (Tajuddin et al. 2011). However, at higher strains, the $\tan \delta$ values increase, indicating that the energy dissipation (viscous behaviour) becomes more significant. The starch solution with 20% glycerol shows the lowest $\tan \delta$ across the tested strains, suggesting that this mixture has the most balanced viscoelastic properties. This balance is critical for applications requiring a material that is both flexible and resistant to deformation (Rodriguez-Gonzalez, Ramsay & Favis 2004). The lower $\tan \delta$ values at 20% glycerol concentration indicate a more elastic-like behaviours, which is desirable for maintaining the integrity of the film or coating during application and subsequent handling (Hager, Vallons & Arendt 2012).

EFFECT OF GLYCEROL CONCENTRATION ON THE GELATINIZATION TEMPERATURE OF PINEAPPLE STEM STARCH SOLUTIONS

In this study, the gelatinization temperature of the starch solutions was analyzed to understand the effects of different glycerol concentrations on the thermal behavior of the starch solution. As shown in Figure 1(e) and Table 1,

the gelatinization temperature of starch solutions exhibited a notable increase at a glycerol concentration of 20%. We observed a significant rise in gelatinization temperature at 20% glycerol, marking the transition of starch from an ordered to a disordered structure. This elevation is likely influenced by the interaction between glycerol and starch molecules (Chen et al. 2017). At this concentration, glycerol appears to strike a balance between disrupting the starch's ordered structure and enhancing the stability of the mixture during heating.

The gelatinization process is crucial as it directly impacts the viscoelastic properties of starch, which are vital for applications such as edible film formation. The observed increase in gelatinization temperature at 20% glycerol suggests that the mixture forms a more robust network, effectively resisting the typical swelling and disintegration of starch granules that occur at lower temperatures. This behavior can be attributed to the plasticizing effect of glycerol, which, at 20% concentration, seems to optimize the internal structure of the starch matrix without compromising its rigidity (Chen et al. 2017).

EFFECT OF CNC CONCENTRATION ON THE RHEOLOGICAL BEHAVIOR OF STARCH

Figure 2(a) illustrates the variation in stress as a function of applied shear rate. Due to the reinforcing nature of CNC, introducing CNC into starch solutions is expected to result in an increase in stress, particularly at higher shear rates. The presence of CNC may disrupt the continuous flow of the starch solution, thereby increasing resistance to deformation and leading to a more pronounced stress response.

Figure 2(b) presents the viscosity variation over the same shear rate range. The addition of CNC results in a shift in the viscosity curve, with viscosity increasing alongside CNC concentration in the starch solution. However, beyond a CNC concentration of 1%, further increases in viscosity become negligible. This increase in viscosity indicates that CNC effectively enhances the internal structure of the starch solution, forming a more resilient and structured matrix that exhibits greater internal friction during flow (El Miri et al. 2015).

Figure 2(c) presents the storage modulus (G') as a function of oscillation strain for starch solutions infused with varying concentrations of CNC. The graph illustrates

TABLE 1. Gelatinization temperatures of starch solutions with different glycerol concentrations

Glycerol content	Gelatinization temperature (°C)
0	83
10	87
20	88
30	86

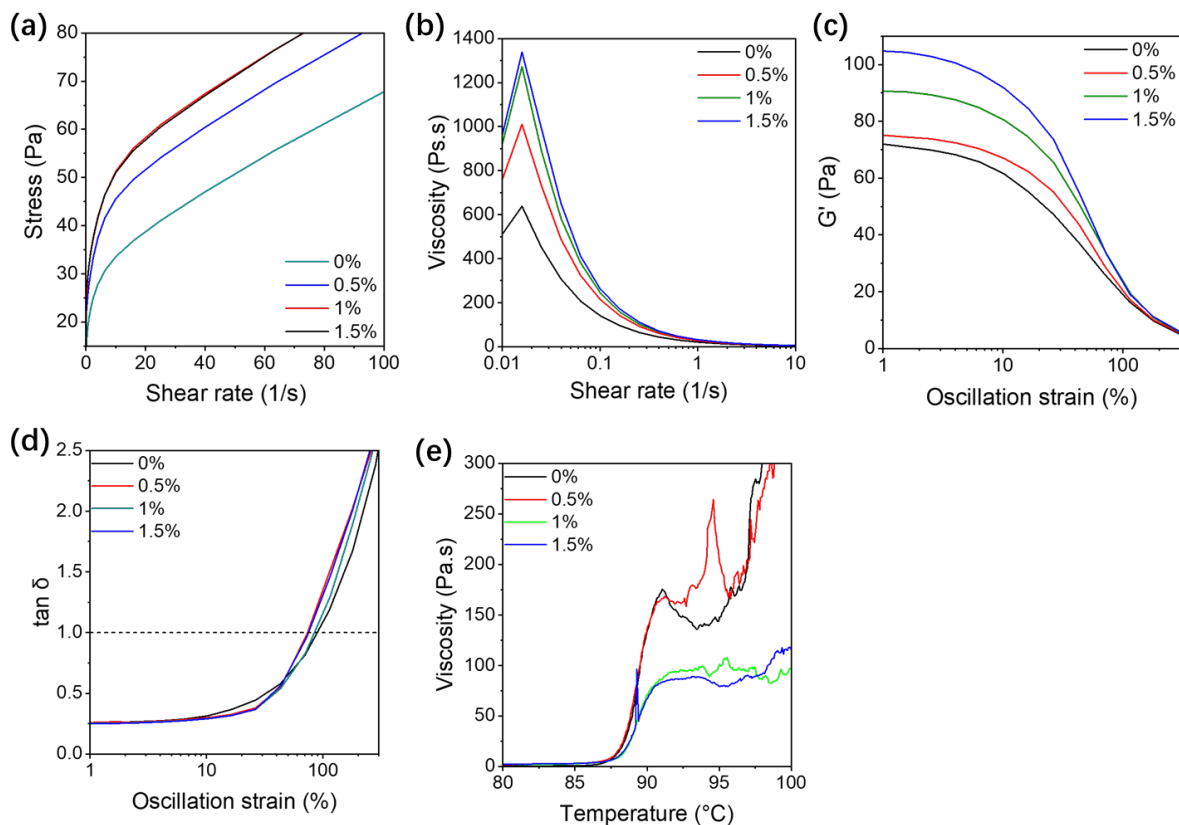


FIGURE 2. (a) Stress response of starch solutions with varying concentrations of CNC as a function of shear rate, (b) Viscosity profiles of starch solutions with varying concentrations of CNC as a function of shear rate, (c) Storage modulus (G') of starch solutions with varying concentrations of CNC, (d) $\tan \delta$ values from oscillation tests of starch solutions with varying concentrations of CNC, and (e) Effect of varying concentrations of cellulose nanocrystals on the gelatinization temperature of starch solutions

a decreasing trend in G' with increasing strain across all concentrations, indicative of the viscoelastic nature of the material. This behavior highlights the absence of a distinct linear viscoelastic region (LVR) where G' would remain constant. Instead, the modulus decreases progressively, reflecting the breakdown of the material's structure under extended deformation. Notably, higher concentrations of CNC correlate with higher initial modulus values, suggesting that CNC effectively reinforces the starch matrix, enhancing its initial elastic response. This reinforcement delays the structural breakdown and prolongs the material's ability to recover, thereby extending its functional range under mechanical stress.

Figure 2(d) shows the variation in $\tan \delta$ values, which represents the ratio of the G'' to the G' of the starch solution. This ratio is indicative of whether the material exhibits more elastic (low $\tan \delta$ values) or viscous (high $\tan \delta$ values) behavior. Our study found that $\tan \delta$ values varied with increasing CNC concentration. At a 1% CNC concentration, elastic behavior was sustained even at

higher strains, reflecting the reinforcing effect of CNC, which enhanced the internal structure and energy storage capacity of the starch matrix (Rosalina & Bhattacharya 2002).

EFFECT OF CNC CONCENTRATION ON THE GELATINIZATION TEMPERATURE OF PINEAPPLE STEM STARCH SOLUTIONS

The effect of varying concentrations of CNC on the gelatinization temperature of starch solutions was investigated. The results indicate that the addition of CNC at different concentrations did not lead to significant changes in gelatinization temperature (Figure 2(e) & Table 2). This suggests that, despite their nanoscale size and potential to interact with the starch matrix, CNC may not significantly disrupt the ordered structure of starch granules required for gelatinization. The interaction between CNC and starch may occur in a manner that does not notably affect the thermal properties governing the gelatinization process.

One possible explanation for these results is that CNC, while enhancing the mechanical properties of the starch matrix through their reinforcing effects, may not alter the hydrogen bonds within the starch granules, which are critical to the gelatinization process. Additionally, the dispersion of CNC might not interfere with the water uptake and thermal penetration necessary for gelatinization to occur.

CHARACTERISTICS OF ZnO-STARCH SOLUTIONS AND FILMS

Figure 3(a) demonstrates the color of the starch solutions with varying concentrations of ZnO, visually supporting the data obtained from the UV-Vis analysis. As the concentration of ZnO increases, the starch solutions become noticeably whiter and brighter. This color change is directly attributable to the increasing presence of the white ZnO particles dispersed within the solution. The enhanced UV absorbance at higher ZnO concentrations can be attributed to the increased presence of ZnO nanoparticles, which are known for their photocatalytic properties and ability to absorb UV light due to their bandgap (Irede et al. 2024). This increased absorption likely results in reduced transmission of UV light through the solution, thereby providing better protection against potential harmful effects of UV radiation (Chouhan et al. 2017).

As shown in Figure 3(b), the absorption peak observed within the 200-400 nm range, characteristic of ultraviolet (UV) light, indicates that ZnO nanoparticles in the starch solution effectively block UV radiation. As the concentration of ZnO increases, this peak becomes more pronounced, suggesting a heightened capacity for UV absorption. The peak reaches its maximum at a 10% ZnO concentration, indicating that this level provides the most effective barrier against UV light among the tested concentrations.

The effectiveness of ZnO at the 10% concentration, as observed in Figure 3, suggests that this ratio represents an optimal balance between ZnO and starch. At this concentration, the ZnO nanoparticles are well dispersed, maximizing the surface area available for UV interaction without aggregation. Aggregation could otherwise scatter light and reduce the overall effectiveness of the solution as a UV barrier (Huang et al. 2019).

The surface morphology of starch films containing different proportions of ZnO was analyzed using Scanning Electron Microscopy (SEM), as depicted in Figure 4. The SEM images show that the films exhibited a less smooth surface, with uniform dispersion of ZnO nanoparticles within the starch matrix. This dispersion indicates effective integration of the ZnO fillers into the starch matrix (Tankhiwale & Bajpai 2012).

The appearance of small dents on the surface of all samples was observed, likely due to water loss during the thermoforming process. The thermoforming process, which

involves heating, causes water to escape from the matrix through steam action. However, the presence of glycerol and starch in the film matrix acts as a plasticizer and creates a barrier, leading to the formation of small pockets on the film surface. These morphological features are indicative of the interaction between the ZnO nanoparticles and the starch matrix, as well as the impact of the processing conditions (Tankhiwale & Bajpai 2012).

The data presented in Table 3 shows that the baseline Water Vapor Transmission Rate (WVTR) for the 0% ZnO control sample is $348.91 \text{ g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$, and the Water Vapor Permeability (WVP) is $0.0127 \text{ g}\cdot\text{m}^{-1}\cdot\text{h}^{-1}\cdot\text{Pa}^{-1}$. As the concentration of ZnO increases, both WVTR and WVP show slight increases. This indicates a marginal decrease in the material's barrier properties to water vapor. Notably, the WVP increases from 0.0127 for the control sample to $0.0157 \text{ g}\cdot\text{m}^{-1}\cdot\text{h}^{-1}\cdot\text{Pa}^{-1}$ for the sample containing 20% ZnO. This trend suggests that the addition of ZnO may slightly impair the material's ability to block water vapor, potentially due to the changes in the microstructure of the starch matrix caused by the incorporation of ZnO nanoparticles.

The comparison of the WVP values is presented in Table 4. The WVP of the starch films in this study, particularly the 5% ZnO control sample, exhibits a value of $0.0144 \text{ g}\cdot\text{m}^{-1}\cdot\text{h}^{-1}\cdot\text{Pa}^{-1}$, aligns closely with some of the reported values. For instance, the study by Tabassi, Moghbeli and Ghasemi (2016) on corn starch films with 9% CNC reports a WVP of $1.277 \times 10^{-6} \text{ g}\cdot\text{m}^{-1}\cdot\text{h}^{-1}\cdot\text{Pa}^{-1}$, which is significantly lower than the values obtained in this study. The study by El Miri et al. (2015) also demonstrates a lower WVP, which may be due to the synergistic effect of carboxymethyl cellulose (CMC) and CNC in the composite film.

The WVP of the potato starch and corn starch film reported by Menzel (2020) and Medeiros Silva et al. (2020) are higher than the values obtained in this study, which could be due to the differences in starch source and the absence of nanoparticles in the film. The pineapple stem starch films with ZnO (2.5 - 20%) from this study show WVP values which are comparable to some of the films in the literature but still indicate a slight increase in WVP due to the addition of ZnO.

EFFECT OF ZnO-ENHANCED STARCH COATINGS ON BANANA RIPENING

Figure 5 illustrates the effect of ZnO concentrations on banana ripening over an 8-day period. The photographs clearly show the progression of ripening in both the control and coated banana samples. The control sample, without any coating, exhibits the typical ripening pattern of bananas, transitioning from green to yellow and then to brown with visible signs of decay by day 4. In contrast, the bananas coated with starch-ZnO solutions demonstrate delayed ripening and reduced discoloration. The

TABLE 2. Gelatinization temperatures of starch solutions with different concentrations of cellulose nanocrystals (CNC)

CNC content (%)	Gelatinization temperature (°C)
0	87.8
0.5	87.7
1	88.1
1.5	88.0

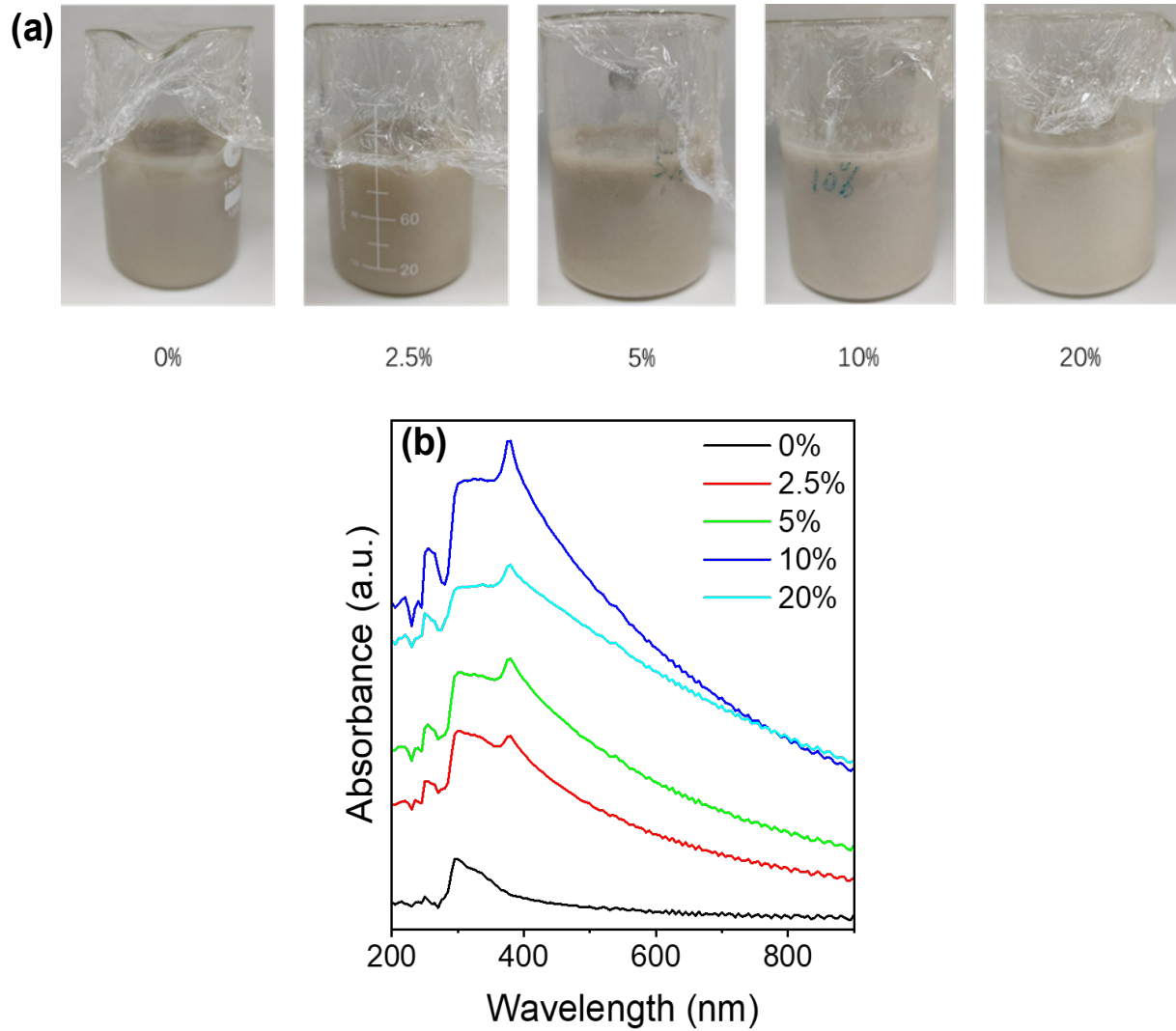


FIGURE 3. Appearance color and UV-Vis results of starch solutions containing different concentrations of ZnO

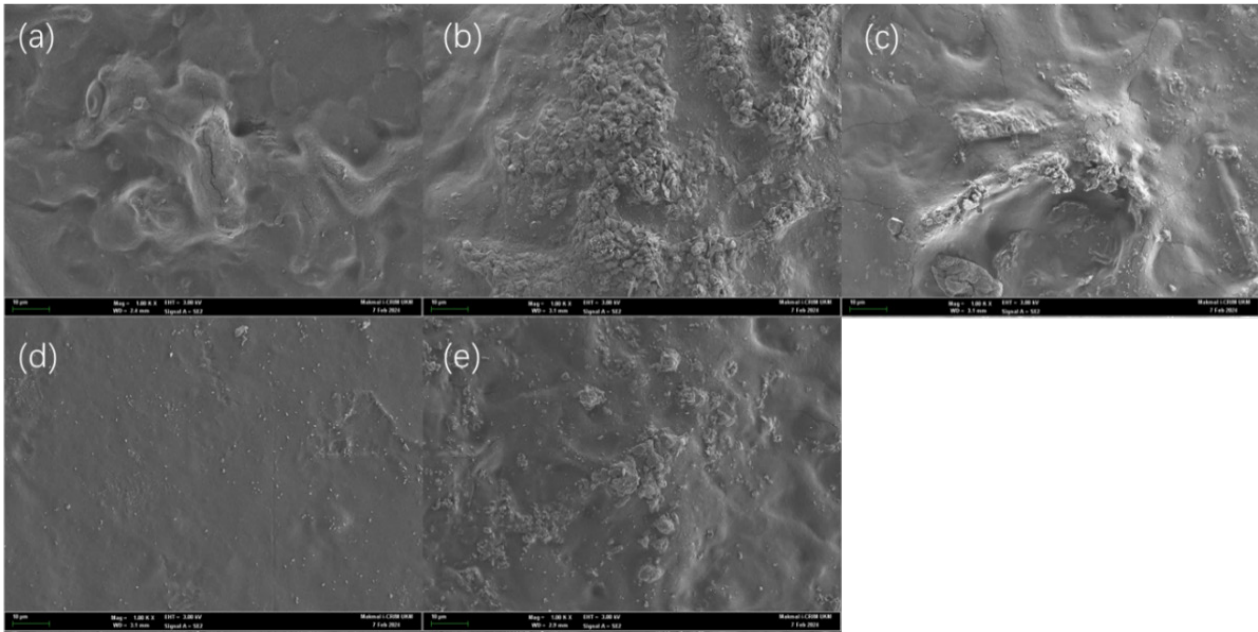


FIGURE 4. SEM images of starch solutions containing different concentrations of ZnO: (a) 0% ZnO, (b) 2.5%, (c) 5%, (d) 10%, and (e) 20% ZnO

TABLE 3. Water vapor transmission rate (WVTR) and water vapor permeability (WVP) of starch films with varying concentrations of ZnO nanoparticles

ZnO (%)	WVTR ($\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$)	WVP ($\text{g}\cdot\text{m}^{-1}\cdot\text{h}^{-1}\cdot\text{Pa}^{-1}$)
0	348.91	0.0127
2.5	349.29	0.0132
5	348.52	0.0144
10	348.66	0.0157
20	348.20	0.0157

TABLE 4. Water vapor permeability (WVP) of films derived from various starch sources

Starch	Testing Condition	WVP	References
Corn starch/9% CNC	30 °C; 50% RH	$1.277 \times 10^{-6} \text{ g}\cdot\text{m}^{-1}\cdot\text{h}^{-1}\cdot\text{Pa}^{-1}$	(Tabassi, Moghbeli & Ghasemi 2016)
Corn starch/CMC/CNC	32 °C; 50% RH	$4.01 \times 10^{-7} \text{ g}\cdot\text{m}^{-1}\cdot\text{h}^{-1}\cdot\text{Pa}^{-1}$	(El Miri et al. 2015)
Corn starch/3% eggshell powder	25 °C	$2.03 \times 10^{-12} \text{ g}\cdot\text{cm}^{-1}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$	(Jiang et al. 2018)
Tapioca starch/35% chitosan nanoparticles	30 °C, 51% RH	$0.63 \times 10^{-11} \text{ g}\cdot\text{m}^{-1}\cdot\text{h}^{-1}\cdot\text{Pa}^{-1}$	(Ruzanna et al. 2022)
Corn starch	38 °C; 90% RH	$0.19 \text{ g}\cdot\text{m}^{-1}\cdot\text{h}^{-1}\cdot\text{Pa}^{-1}$	(Medeiros Silva et al. 2020)
Potato starch	25 °C, 53-100% RH	$0.118 \text{ g}\cdot\text{m}^{-1}\cdot\text{h}^{-1}\cdot\text{Pa}^{-1}$	(Menzel 2020)
Pineapple stem starch/5% ZnO	25.5 °C, 75% RH	$0.0144 \text{ g}\cdot\text{m}^{-1}\cdot\text{h}^{-1}\cdot\text{Pa}^{-1}$	This study

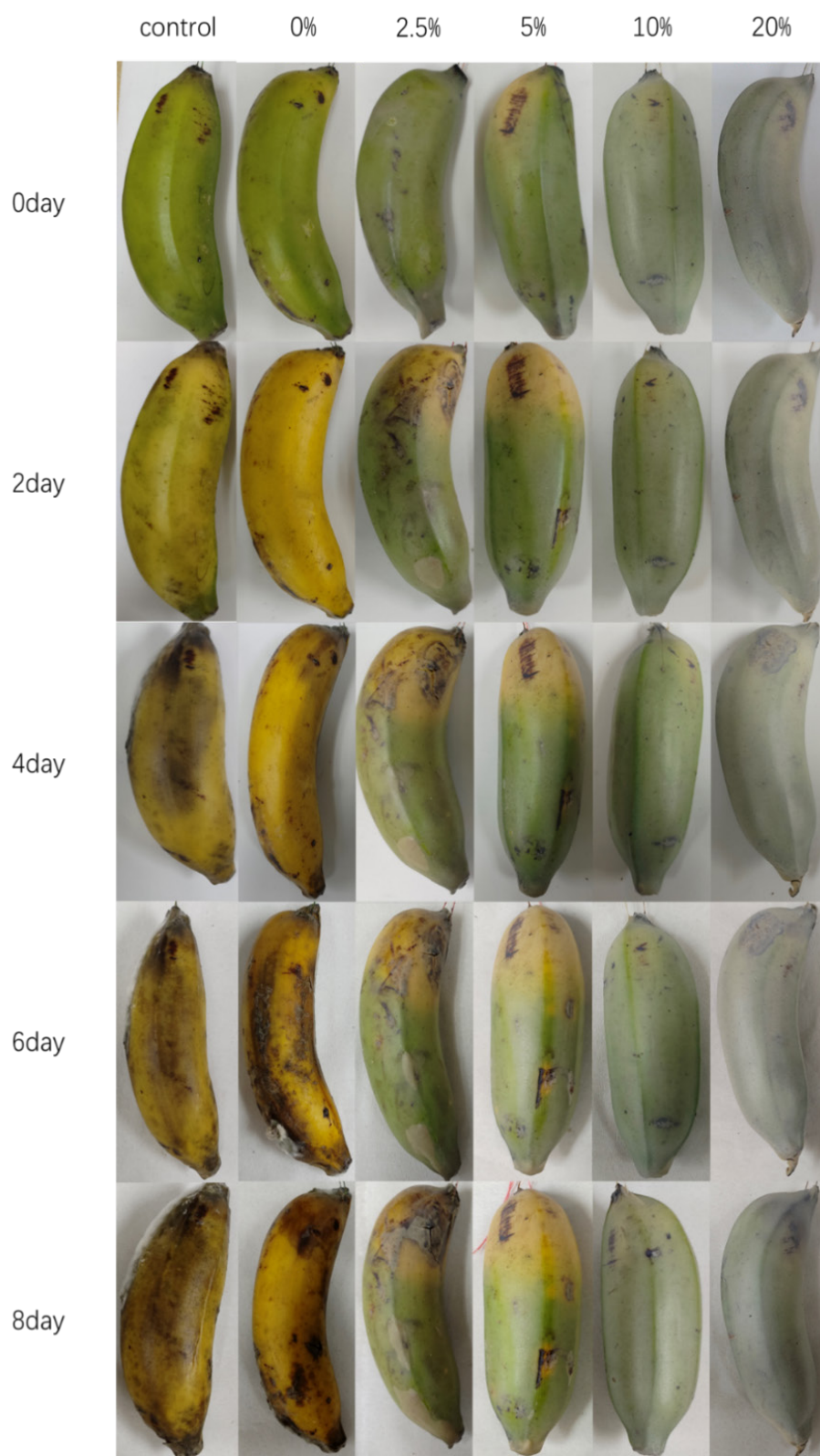


FIGURE 5. Effect of ZnO-enhanced starch coatings on the ripening process of bananas over an 8-day period

effectiveness of the coating appears to be directly related to the ZnO concentration. Bananas coated with higher ZnO concentrations (10% and 20%) retain their green color and firmness for a longer duration, exhibiting minimal signs of ripening even after 8 days. This observation suggests that higher concentrations of ZnO in the coating provide a more effective barrier against the factors that promote ripening.

The delayed yellowing observed in the bananas coated with the ZnO-enhanced starch solution can also be attributed to ZnO's UV-absorbing properties, as shown in Figure 3(b). These properties help protect the bananas from photo-oxidation reactions, which are responsible for the yellowing when the fruit is exposed to light (Mertins et al. 2015). By incorporating ZnO into starch-based coating packaging, a protective layer is formed around the bananas. This layer mitigates the effects of light exposure, which is a critical factor in both the ripening and decay of the fruit, thereby extending the shelf life of the bananas.

CONCLUSIONS

This research demonstrated the successful development of pineapple stem starch-based films enhanced with cellulose nanocrystals (CNC) and zinc oxide (ZnO) nanoparticles, which significantly improved the film's functional properties. The incorporation of CNC enhanced the mechanical and rheological properties of the films, making them more resilient and structured. Additionally, ZnO nanoparticles imparted effective ultraviolet (UV) blocking capabilities, crucial for delaying the ripening and decay of perishable fruits such as bananas. The study highlights the potential of using agricultural waste materials like pineapple stems to create sustainable packaging solutions that not only preserve food quality but also reduce environmental impact. The promising results suggest that these multifunctional films could be a viable alternative in the food packaging industry, contributing to extended shelf life and reduced food waste.

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