

Article

Tailoring Polyvinyl Alcohol/Carnauba Wax Film Properties Through Plasticizer Selection: A Pathway to Optimized Biodegradable Materials

Abodunrin Tirmidhi Tijani ¹ and Ademola Monsur Hammed ^{2,*} ¹ Environmental and Conservation Sciences, North Dakota State University, Fargo, ND 58102, USA; abodunrin.tijani@ndus.edu² Agricultural and Biosystems Engineering, North Dakota State University, Fargo, ND 58102, USA

* Correspondence: ademola.hammed@ndsu.edu

Abstract

Polyvinyl alcohol (PVA)-based films are promising biodegradable alternatives to petroleum-derived plastics; however, their high rigidity and moisture sensitivity limit practical applications. In this study, PVA/carnauba wax (CW) films were prepared via solution casting and systematically modified using four plasticizers: glycerol (GLY), sorbitol (SOR), glucose (GLU), and sucrose (SUC), at concentrations of 0.1–0.5% (*v/w*, relative to PVA). Thermal analysis showed that GLY and SOR effectively reduced the glass transition temperature from 52.35 °C (control) to as low as 49.14 °C (0.2% GLY) and 50.70 °C (0.4% SOR), while SUC and SOR plasticized films exhibited improved thermal stability, with the highest melting temperature observed for 0.3% SUC (80.6 °C). SEM micrographs revealed that GLY at moderate concentrations (0.2–0.3%) produced the most homogeneous film morphology, whereas SUC at higher concentrations led to surface roughness and phase separation. Water contact angle measurements showed increased surface hydrophobicity at low plasticizer contents, with 0.1% GLY and 0.2% GLU exhibiting contact angles above 100° compared to the control film (<90°). Mechanical testing demonstrated that SUC at 0.2% had the highest tensile strength (3.03 MPa) compared to 0.73 MPa (control), while GLY at 0.3% yielded the highest elongation at break (9.26%), compared to 0.62% for the unplasticized film. These results demonstrate that precise control of plasticizer type and concentration enables effective tuning of PVA/CW film properties, offering a viable strategy for designing biodegradable films tailored for packaging and agricultural applications.

Keywords: plasticization; sustainable polymers; thermal stability; biodegradable packaging



Academic Editor: Roberto Pantani

Received: 7 February 2026

Revised: 25 February 2026

Accepted: 1 March 2026

Published: 3 March 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

1. Introduction

Plasticizers have been extensively utilized since the early 19th century to enhance the durability and processability of polymers. These compounds, characterized by their low molecular weights and non-volatile nature, play a critical role in improving the elasticity and workability of materials, particularly plastics and elastomers [1]. The Council of the International Union of Pure and Applied Chemistry (IUPAC) defined a plasticizer as a substance or material incorporated in a material (usually a plastic or elastomer) to increase its flexibility, workability, or distensibility [2]. Global production of plasticizers has reached approximately 5 million tons annually over the past decade, with applications in approximately 60 polymers and more than 30 product categories.

In recent years, there has been increased focus on the use of natural-based plasticizers, driven by the demand for bio-based materials derived from renewable and biodegradable resources to mitigate the use of conventional plastic products [3]. The effectiveness of plasticizers is predominantly influenced by factors such as molecular weight, size, and the number of functional groups capable of interacting with the host polymer. Plasticizers function by occupying intermolecular spaces between polymer chains, thereby reducing secondary forces (e.g., hydrogen bonding and van der Waals interactions) and altering the three-dimensional organization of polymers. This results in increased free volume and molecular mobility, facilitating enhanced flexibility and processability. Compatibility between a polymer and a plasticizer depends on polarity, hydrogen bonding capability, and solubility parameters, which together govern plasticizer dispersion and performance within the polymer matrix.

Biodegradable films made from polyvinyl alcohol (PVA) have gained substantial attention as potential biomaterials and sustainable packaging materials due to PVA's excellent film-forming ability, biodegradability, and nontoxicity. However, neat PVA films exhibit significant limitations, such as high rigidity, brittleness, and sensitivity to moisture, which restrict their utility without careful formulation. To address these shortcomings, researchers have investigated the incorporation of hydrophobic additives such as carnauba wax (CW) and plasticizers like glycerol to improve water resistance and mechanical performance in PVA films [4,5]. The choice of plasticizer critically influences film characteristics. Glycerol, sorbitol, and other polyols remain among the most studied plasticizers for PVA due to their strong ability to form hydrogen bonds with PVA's abundant hydroxyl groups. Recent work has revealed that glycerol significantly alters PVA's crystallinity and surface morphology, reducing crystalline domains and enhancing chain mobility [6]. Conventional polyols, however, often present trade-offs: while they increase flexibility and elongation, they may also elevate water vapor permeability and decrease thermal stability. These phenomena have been observed across multiple biodegradable polymer systems, including PVOH/starch chitosan blends, where plasticizer content was found to modulate mechanical and barrier properties in a concentration-dependent manner [7]. Various types of plasticizers have been employed, particularly with biopolymers, including water, glycerol, sorbitol, xylitol and monosaccharides. The effects of different plasticizers and their concentrations on the properties of films have been extensively investigated. These studies have demonstrated that plasticizer type and concentration can significantly influence mechanical properties, water vapor permeability, thermal stability, and other characteristics of polymer-based films [8–18].

The selection of glycerol (GLY), sorbitol (SOR), glucose (GLU), and sucrose (SUC) as plasticizers in this study is grounded in their systematic variation in molecular architecture and functional group density. GLY is a small triol with high mobility and three hydroxyl groups, enabling efficient penetration between PVA chains and strong hydrogen-bonding interactions. SOR, a linear hexitol, possesses six hydroxyl groups and a longer carbon backbone, which increases molecular size, reduces diffusion, and can promote stronger but less mobile intermolecular associations. In contrast, GLU and SUC represent monosaccharide and disaccharide sugars, respectively, characterized by cyclic ring structures and higher molecular weights. Their rigid conformations and extensive hydroxyl functionality can generate dense hydrogen-bond networks, potentially increasing intermolecular cohesion and influencing crystallinity differently than flexible polyols [19]. Comparing these molecules therefore allows systematic evaluation of how chain length, molecular flexibility, hydroxyl density, and structural rigidity influence plasticization efficiency, phase compatibility, and interfacial behavior in PVA/CW systems.

Furthermore, the distinction between polyols and sugars is particularly relevant in multiphase polymer–lipid systems. Polyols generally exhibit greater conformational flexibility and lower glass transition temperatures, favoring plasticization through increased free volume and chain mobility [20]. Sugars, by contrast, often display higher glass transition temperatures and stronger intermolecular cohesion, which may restrict chain motion yet enhance film strength or barrier performance. In the presence of CW, these structural differences may also affect the distribution of plasticizer molecules between hydrophilic and hydrophobic domains, thereby modulating dispersion of wax particles, interfacial adhesion, and overall film morphology. Understanding how these molecular-level characteristics translate into macroscopic film properties is essential for rational formulation design.

Despite recent investigations of individual plasticizers in PVA-based films, most prior studies have focused on single-plasticizer systems or general modification strategies. Comparative, systematic evaluation of structurally distinct plasticizers within PVA/CW blends remains limited. There is insufficient understanding of how plasticizer chemistry influences the coupled mechanical, thermal, and hydrophilic properties of films containing both hydrophilic polymer and hydrophobic wax phases. Elucidating these relationships is critical for tailoring performance attributes such as flexibility, tensile strength, thermal stability, and moisture resistance.

Therefore, this study aims to systematically investigate the effects of multiple plasticizers and their concentrations on the properties of PVA/CW films, with a focus on elucidating how plasticizer chemistry and content influence mechanical strength, flexibility, thermal behavior, hydrophilicity, and other functional characteristics. By integrating insights from recent studies with comprehensive experimental evaluation, the present work seeks to fill an important knowledge gap in the development of sustainable, bio-based film materials for packaging and related applications.

2. Methods

2.1. Materials

PVA (average Mw 31,000 g/mol, 98–99% hydrolyzed mp: >300 °C) was obtained from SigmaAldrich (St. Louis, MO, USA), Carnuba wax powder (mp: 82–86 °C) obtained from Thermo Fisher Scientific, Madison, WI, USA, Stearic acid powder (FW 284.48) and Sorbitol $\text{HOCH}_2(\text{CHOH})_4\text{CH}_2\text{OH}$ from J.T Baker, Phillipsburg, NJ, USA, Polysorbate 20 ($\text{C}_{58}\text{H}_{114}\text{O}_{26}$, MW: 11,227.53) from VWR chemicals, Solon, OH, USA, glucose $\text{C}_6\text{H}_{12}\text{O}_6$ (FW: 180.16) obtained from Macron Fine Chemicals, Radnor, PA, USA, Sucrose $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ (FW: 342.30) from EMD, Boston, MA, USA, and glycerol ($\text{C}_3\text{H}_8\text{O}_3$) (Figure 1).

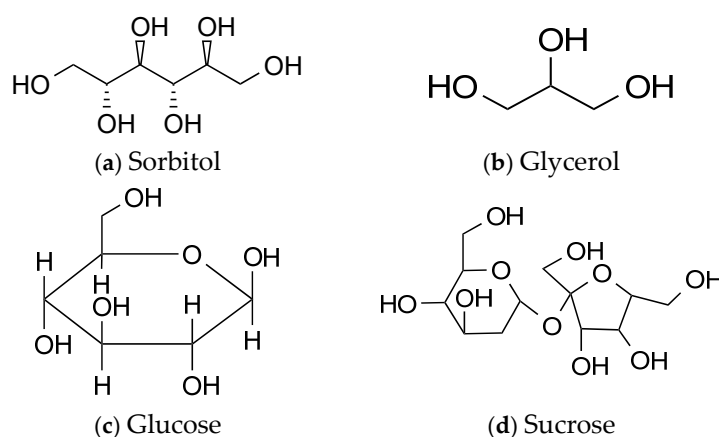


Figure 1. Chemical Structure of different plasticizer types.

2.2. Preparation of PVA/CW Films

PVA-based films were prepared using the solution casting technique, with slight modifications from previous studies [1]. A 10% (*w/v*) PVA aqueous solution was prepared in 50 mL distilled water in a beaker. The mixture was heated at 85 °C and stirred continuously at 500 rpm for 20 min in a water bath to obtain a homogeneous solution. Next, 0.3 mL of polysorbate 20 (emulsifier) was added to the hot PVA solution and stirred for 5 min. In a separate container, 40 wt% CW/SA relative to the PVA was melted and added to the homogenous PVA solution at 120 °C with continuous stirring in a water bath for 45 min. The plasticizers, GLY, SOR, GLU, and SUC, were used at concentrations of 0.1, 0.2, 0.3, 0.4, and 0.5% (*v/w*). A PVA/CW film without plasticizers was made as a control. The film-forming solution was stirred in a water bath for 20 min to ensure its homogeneity. The solution was allowed to cool for a while and 15 mL each of the solution was then poured on a clean, leveled glass plate and allowed to dry for 48 h at room temperature (20–25 °C). The dehydrated films were peeled from the casting plates and stored in a desiccator at $53 \pm 1\%$ relative humidity (RH) inside plastic bags before characterization. The film preparation procedure is illustrated in Figure 2.

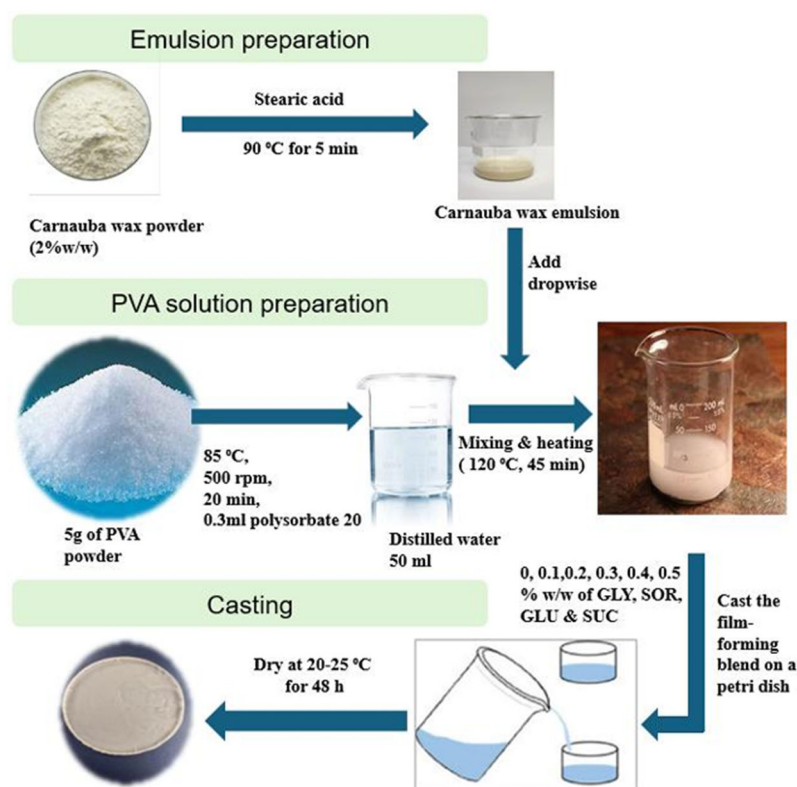


Figure 2. Film preparation scheme.

2.3. Characterization of PVA/CW Blends

2.3.1. Fourier-Transformed Infrared Spectroscopy (FT-IR)

FTIR analysis was performed to identify changes in surface functional groups following plasticizer incorporation. Spectra were collected using a Nicolet 8700 FTIR Spectrometer (Thermo Fisher Scientific, Madison, WI, USA) operated with OMNIC™ software (OMNIC SST 88.1, Thermo Fisher Scientific) in the range of 4000–500 cm^{-1} during 128 scans at a resolution of 4 cm^{-1} . An empty-beam (air) background spectrum was collected prior to sample acquisition and automatically subtracted by the software. Spectra were baseline-corrected prior to interpretation.

2.3.2. Tensile Test

An Instron model 5542 universal testing machine (Norwood, MA, USA) was used to carry out tensile tests of plasticized and unplasticized PVA/CW films with a load cell of 1 kN. The parameters of the PVA/CW films, conditioning, and tensile testing were performed in accordance with ASTM D-882 [21]. Initial grip separation and crosshead speed were set at 3 cm and 10 mm/min, respectively. The samples were cut into strips with a width of 15 mm and had an effective length of 50 mm between the clamps at the beginning of the measurement [22]. To measure the tensile properties as a function of the thickness, the thickness of each specimen was measured. For each specimen, five-fold determination was performed and the arithmetic mean and standard deviation was calculated. The tensile strength (MPa), elongation at break (%), and Young's modulus of elasticity (MPa) results for each sample are also presented as mean and standard deviation.

2.3.3. Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA)

The weight loss as a function of temperature was depicted as a thermal-gravimetric analysis curve using the TRIOS software (v5.1.1.46572). The tests were performed in the temperature range of 20–600 °C at a heating rate of 10 °C/min under nitrogen gas using a TGA 550 instrument (TA Instruments, New Castle, DE, USA). The glass transition temperature (T_g) and melting temperature (T_m) of the PVA/CW and PVA/CW/plasticizer blend films were analyzed using TA DSC 2500 thermal instrument (TA Instruments New Castle, DE, USA). The film samples 2.0 (2.5 mg) were sealed in an aluminum crucible and heated from room temperature to 120 °C at a heating rate of 10 °C/min under an inert nitrogen gas atmosphere (50 mL/min) to prevent thermal oxidation of the polymer samples. The glass transition temperature was taken as the midpoint of the heat capacity change. The melting temperature (T_m) of each sample was determined from the melting peak area.

2.3.4. Scanning Electron Microscopy (SEM)

The surface morphologies of the PVA/CW/GLY-SOR-GLU-SUC blends were evaluated using a JEOL JSM-6490LV variable-pressure SEM (JEOL USA, Peabody, MA, USA). The specimens were coated with a gold layer using a sputter-coater (Polaron SC7640, Quorum Technologies Ltd., Lewes, UK) and operated at an accelerating voltage of 15 kV and magnifications of 1500 $\times$.

2.3.5. Water Contact Angle

Contact angles were measured with water, employing the sessile drop method at 2°, the temperature of the environment set at 23 °C, a needle width of 0.525 mm, and a drop size of 5 mL using the DSA 100, KRÜSS (Hamburg, Germany). The measurements were done in triplicate and analyzed using ADVANCE® software (v3.18.5).

2.3.6. Film Solubility in Water

Representative samples ($n = 3$) at 2 cm $\times$ 2 cm were obtained from each film and dried in an oven at 105 °C for 24 h. The samples were weighed to determine the initial dry matter of each film (W_1). Each sample was immersed in 30 mL of distilled water and kept at 23 ± 2 °C for 3 h. The sealed beaker was stirred periodically [23]. The insoluble portion of film sample was removed from the soluble matter in distilled water and dried at 105 °C for 24 h. The dried samples were reweighed to know the weight of the solubilized dry matter (W_2). Water solubility of each film was determined by Equation (1):

$$\text{Solubility (\%)} = \frac{w_1 - w_2}{w_1} \times 100 \quad (1)$$

where w_1 is weight of initial dry film and w_2 is weight of undissolved film.

2.3.7. Statistical Analysis

Microsoft® Excel® for Microsoft 365 MSO (Version 2601 Build 16.0.19628.20214) and OriginPro 2026 SR1 10.3.0.197 were used for all statistical analysis. Two-way analysis of variance (ANOVA) was conducted to evaluate the effect of formulation on the measured response variables at a significance level of $\alpha = 0.05$ (see Supplementary Materials). All results are reported as mean $\pm$ standard deviation based on triplicate measurements.

3. Results and Discussion

3.1. Fourier-Transform Infrared Spectroscopy

The FTIR spectra of PVA/CW films with increasing concentrations of GLY, SOR, GLU, and SUC in Figure 3 reveal significant structural interactions between the polymer matrix and the additives. The primary changes observed occur in the hydroxyl (O-H) stretching region (3200–3500 cm^{-1}) and carbonyl (C=O) stretching region (1700–1750 cm^{-1}). For PVA/CW plasticized films, a shift of the (O-H) stretching vibration band from 3281.55 cm^{-1} for unplasticized PVA/CW to slightly higher wavenumbers are observed when increasing the concentration for all the plasticizer types (up to 3297.80 cm^{-1} for 0.5% GLY, 3296.70 cm^{-1} for 0.5% SOR, 3296.07 cm^{-1} for 0.5% GLU, and 3295.76 cm^{-1} for 0.5% SUC, respectively). A possible reason for this effect is the dissociation of hydrogen bonds between the PVA chains and the formation of new hydrogen bonds between the PVA and plasticizer molecules. Studies have consistently shown that plasticizers increases the chain mobility of PVA and starch-based films but can also compromise water resistance [8,11,15–18].

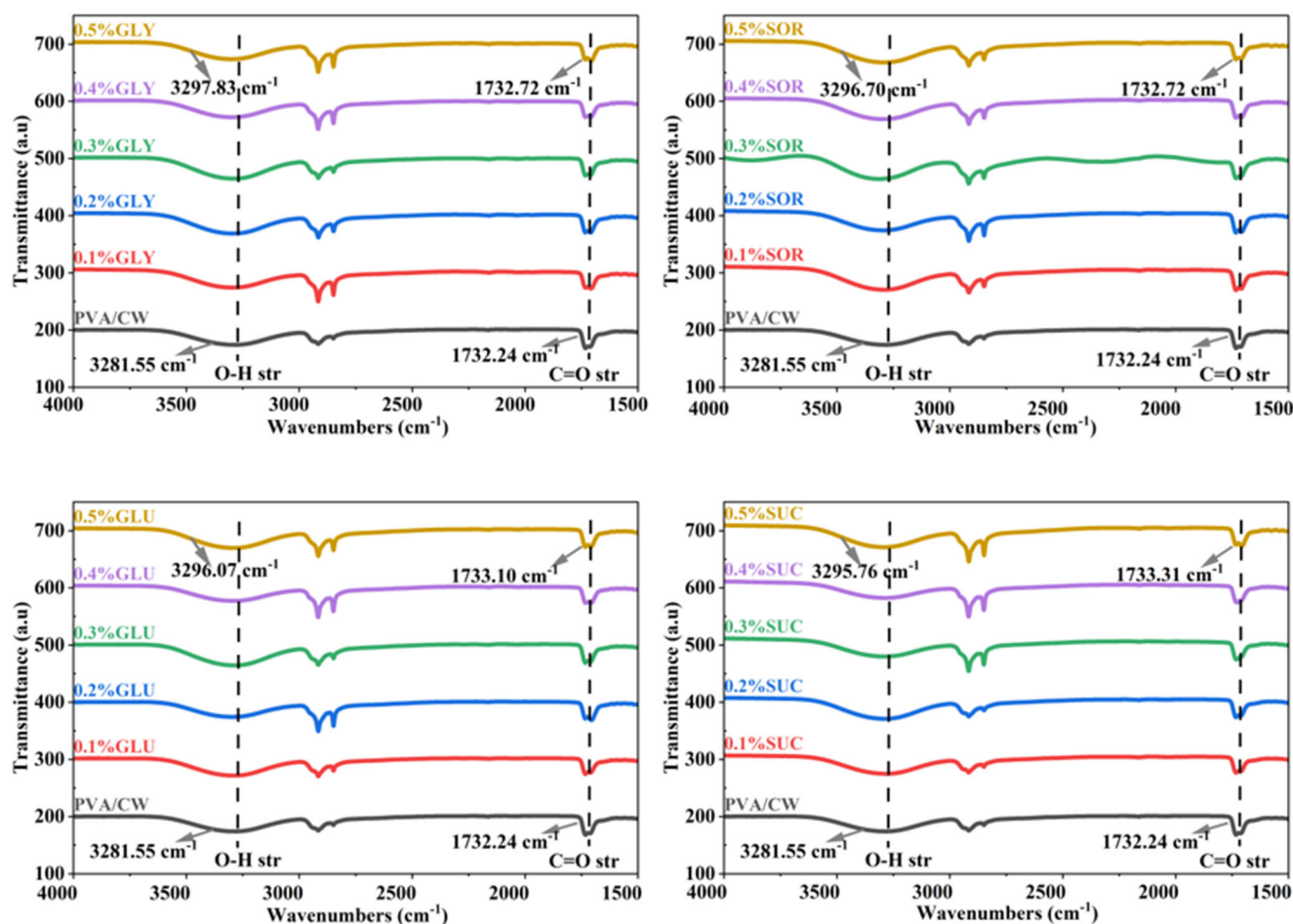


Figure 3. FTIR spectra of the PVA/CW films for increasing GLY, SOR, GLU, and SUC concentrations.

Unlike SOR with larger molecular size and partial crystallinity which results in less mobility and lower plasticizing efficiency, GLY is smaller in size with high hydroxyl functionality. As a result, SOR has been reported to enhance the toughness and reduce the brittleness of biopolymer films while contributing less to moisture uptake than GLY [14,24]. It was noticed as well that the peaks at around 1700 cm^{-1} corresponding to a carbonyl (C=O) group presented identical spectra peaks for all the films compared to the control regardless of plasticizer type and concentration. This indicates that the plasticizers have similar functional groups, and they are all categorized as polyols. This observation is similar to the findings by [25], when the effect of fructose, SOR and urea on the physical, morphological, and thermal characteristics of cornstarch-based films was assessed.

3.2. Gravimetric Analysis

Thermogravimetric analysis (TGA) of the PVA/CW and plasticizer films was performed to determine their thermal stability and degradation. All plasticized films exhibited three distinct weight losses in their thermal degradation, as shown in Figure 4. The results demonstrate how increasing concentrations of GLY, SOR, GLU, and SUC influence the thermal properties of PVA/CW films. In general, the thermograms show a multi-step degradation process, where the initial weight loss ($\sim 100\text{--}150\text{ }^{\circ}\text{C}$) is attributed to moisture evaporation, while the major thermal decomposition occurs between $200\text{--}350\text{ }^{\circ}\text{C}$, corresponding to polymer degradation. As plasticizer concentration increases, the thermal stability of the films decreases, particularly for GLY and GLU plasticized films (Figure 4a,c). The onset of thermal degradation shifts to lower temperatures with higher plasticizer content, indicating that these plasticizers disrupt polymer chain interactions, leading to earlier breakdown. This trend is particularly evident for GLY, which, due to its small molecular size and high hydrophilicity, weakens the intermolecular forces within the PVA matrix, reducing the energy required for thermal decomposition. In contrast, SOR and SUC plasticized films (Figure 4b,d) exhibit a relatively smaller reduction in thermal stability with increasing concentration. This suggests that SUC and SUC form stronger hydrogen bonds with PVA, helping to maintain the polymer's structural integrity at higher temperatures. The delayed degradation onset at higher SOR and SUC concentrations implies that these plasticizers provide some thermal stabilization by restricting molecular motion and enhancing intermolecular interactions. However, at excessively high concentrations, even these plasticizers begin to show a gradual reduction in thermal stability, though not as pronounced as GLY and GLU. Overall, the thermogram analysis confirms that while plasticizers improve flexibility, they generally reduce the thermal resistance of the films, with sorbitol and sucrose providing better thermal stability compared to GLY and GLU.

From these results, SOR and SUC emerge as the better plasticizers in terms of thermal performance, with moderate concentrations (0.2–0.4%) providing an optimal balance between plasticization and stability.

3.3. Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) provides valuable information about the thermal properties of films. Film DSC analysis enables the identification and characterization of different phases or transitions within the film in response to temperature change. Figure 5 shows the main thermal parameters obtained by differential scanning calorimetry (DSC) which include film's glass transition temperature (T_g) and melting temperature (T_m). The thermal behavior of the polymer films in this study demonstrates the influence of plasticizers on the T_g and T_m . Compared to the control sample ($T_g = 52.35\text{ }^{\circ}\text{C}$, $T_m = 79.03\text{ }^{\circ}\text{C}$), the addition of GLY and SOR led to a notable reduction in T_g , with the lowest values observed for 0.2% GLY ($49.14\text{ }^{\circ}\text{C}$) and 0.4% SOR ($50.7\text{ }^{\circ}\text{C}$), indicative of a strong plasticizing effect.

This trend is consistent with previous studies on PVA and other hydrophilic polymers, where GLY and SOR act as effective plasticizers by increasing free volume and molecular mobility [26–31]. The T_m values for GLY modified films remained stable (~ 78 – 79.5 °C), whereas SOR slightly decreased T_m , suggesting minor structural changes in crystallinity. Similar studies have reported that GLY exhibits a stronger T_g -lowering effect than SOR, likely due to its lower molecular weight and higher hydrogen bonding interactions with the polymer matrix [14,15,18,32,33].

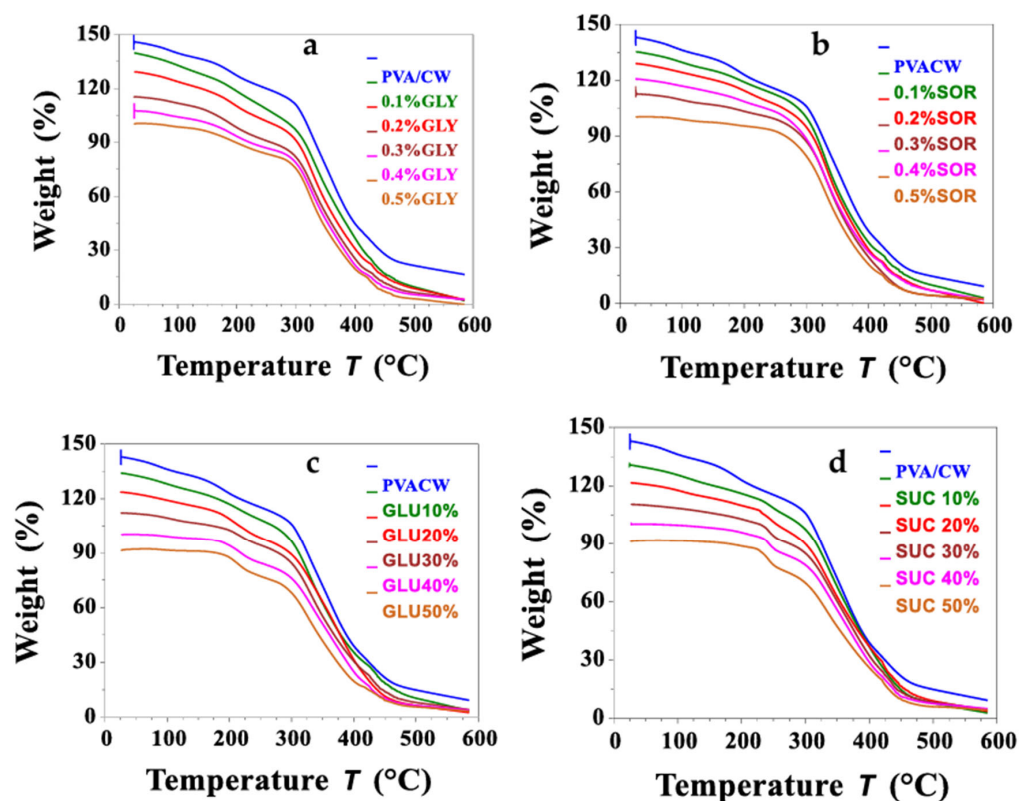


Figure 4. Thermograms of: (a) GLY-plasticized films, (b) SOR-plasticized films, (c) GLU-plasticized films, and (d) SUC-plasticized films.

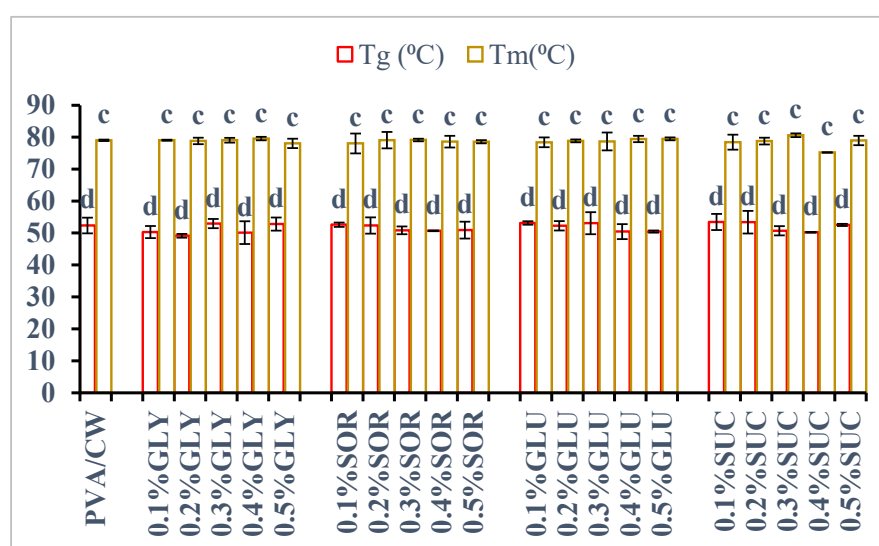


Figure 5. Glass transition temperature (T_g) and Melting temperature (T_m) of the films. Values represent mean $\pm$ SD. Bars with the same letter are not significantly different ($p > 0.05$) (see Supplementary Materials Table S1).

Conversely, GLU and SUC exhibited a relatively weaker plasticization effect, with T_g values remaining above 50 °C for most concentrations. Notably, 0.1% SUC (53.46 °C) and 0.2% SUC (53.38 °C) even showed higher T_g than the control, suggesting limited disruption of intermolecular forces. This aligns with prior research indicating that larger, less mobile sugar molecules like SUC exhibit restricted interaction with polymer chains, leading to reduced efficiency in lowering T_g . Additionally, the slight increase in T_m for 0.3% SUC (80.6 °C) suggests a possible crystallization effect, reinforcing the idea that SUC might promote structural ordering rather than plasticization. These results align with past findings on carbohydrate-based plasticizers, where monosaccharides (e.g., GLU) show intermediate effects, while disaccharides (e.g., SUC) may even enhance rigidity [34–36]. Overall, among all formulations, the PVA/CW film containing 0.3% SUC exhibited the highest thermal stability as evidenced by its T_m of 80.6 °C, while GLU plasticized films showed consistently high T_g values and stable melting behavior, indicating superior thermal resistance compared to GLY and SOR plasticized films.

3.4. Scanning Electron Microscopy (SEM)

The microstructure of the film surfaces was examined to determine the difference in surface morphology caused by plasticizer type and concentration. Figure 6 provides the (SEM) images which reveal significant morphological changes in the plasticized films upon the addition of different plasticizers (GLU, GLY, SOR, and SUC) at varying concentrations (0.1–0.5%). The control film exhibits a relatively smooth and compact surface, indicating a rigid and brittle structure. As plasticizers are incorporated, the films show varying degrees of roughness and phase separation, depending on the type and concentration used. 0.1–0.5% GLU plasticized films display a relatively smooth surface at lower concentrations, but as the concentration increased to 0.5%, the surface becomes more irregular, suggesting increase in molecular mobility and phase separation. Similarly, glycerol-based films 0.1% GLY to 0.5% GLY also show a smooth and homogenous structure, indicating strong polymer–plasticizer interactions that enhance film flexibility. However, at higher concentrations, minor phase separation appears. The result from this investigation is different from a study on the effect of GLY and SOR on the physical properties of biodegradable films based on sugar palm starch that reported homogenous, compact, and dense film surfaces upon further increase of plasticizer concentrations [17]. 0.1% SOR to 0.5% SOR and sucrose (0.1% SUC–0.5% SUC) plasticized films show more heterogenous surfaces, particularly at higher concentrations. SOR plasticized films exhibit a moderate increase in roughness with increasing concentration, suggesting a controlled plasticization effect that maintains structural integrity. SUC plasticized films, on the other hand, display significant phase separation and a rougher surface, particularly at higher concentrations, indicating poor miscibility with the polymer matrix.

Phase separation in the PVA/CW films is primarily governed by plasticizer polarity, molecular size, and hydrogen-bonding capability, which determines their miscibility with the polymer matrix. Because PVA is highly hydrophilic while carnauba wax is hydrophobic, the blend is intrinsically prone to microphase separation, and plasticizers influence this balance by modifying intermolecular interactions. GLY, a small and highly polar triol, disperses uniformly and forms strong hydrogen bonds with PVA chains, resulting in smooth and homogeneous morphologies at low concentrations; slight heterogeneity at higher levels is attributed to GLY self-association [18]. In a similar pattern GLU exhibits similar polarity but its larger cyclic structure limits diffusion, leading to aggregation and surface irregularities as concentration increases. SOR, with higher molecular weight, shows partial compatibility and moderate roughness due to reduced mobility and competing SOR–SOR interactions. In contrast, SUC displays pronounced phase separation because

its bulky disaccharide structure and strong self-association hinder uniform dispersion, producing large domains and rough surfaces [13]. Overall, the observed morphology trend (GLY > GLU > SOR > SUC in compatibility) reflects decreasing molecular mobility and increasing steric hindrance, confirming that plasticizers with smaller size and stronger polymer interactions yield more homogeneous films.

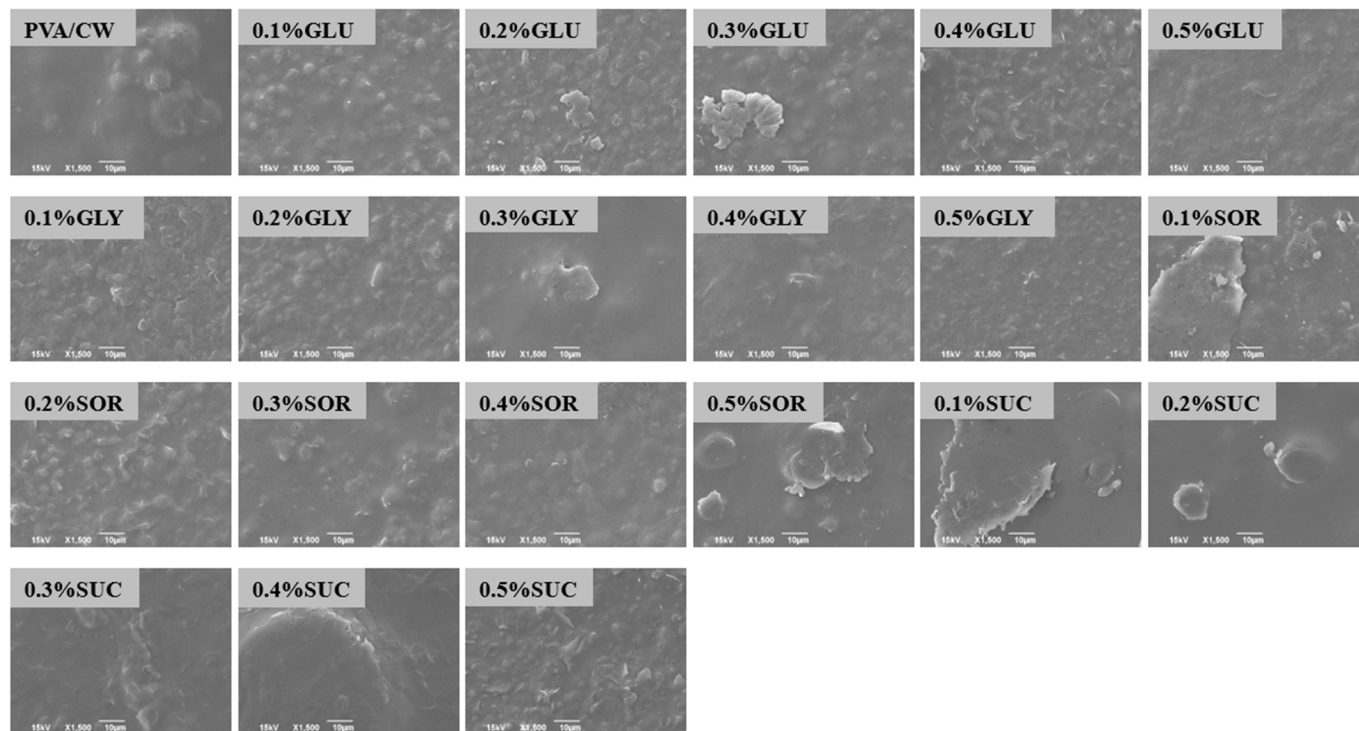


Figure 6. SEM images of PVA/CW films with various plasticizers type and concentration.

Based on the SEM analysis, GLY at moderate concentrations (0.2% and 0.1%) appears to be the most effective plasticizer, as it provides a smooth, homogeneous structure with minimal phase separation. GLU at lower concentrations (0.1% and 0.2%) also maintains a relatively smooth structure, making it a good alternative for applications requiring moderate plasticization.

3.5. Water Contact Angle

This is a key parameter used to measure the wettability of a surface, indicating how a liquid interacts with a solid material. Typically, a high contact angle ($>90^\circ$) suggests low wettability where the liquid does not spread easily. On the other hand, a low contact angle ($<90^\circ$) indicates hydrophilic behavior and high wettability. Figure 7 shows that the control sample PVA/CW has a relatively lower contact angle compared to some of the plasticized films. A two-way ANOVA was performed to evaluate the effects of plasticizer type and concentration on PVA/CW films. Results showed that the concentrations and types of plasticizers had no statistical significant ($p > 0.05$) effect on the film's surface wettability. Although certain formulations show visible trends in the plotted mean values, the within-group variability resulted in non-significant statistical outcomes. However, when plasticizers were introduced, GLY and GLU initially increased hydrophobicity at lower concentrations (0.1% GLY, 0.2% GLY and 0.1% GLU, 0.2% GLU) with contact angles above 100° , respectively. A decline in higher concentrations of these plasticizers was observed, suggesting that their impact diminishes beyond a certain threshold. In a previous study, the addition of different hydrophilic plasticizers such as GLY, ethylene glycol, and polyethylene glycol to chitosan films reported a decrease in hydrophobicity of the film

surfaces. The higher hydrophilicity of the samples was attributed to the hygroscopicity (the water binding capacity) of the plasticizer [37]. It was also reported in another study that investigated how different GLY concentrations affect the structural and surface properties of starch films that higher GLY content resulted in a reduced contact angle and increased hydrophilicity [9]. Conversely, there was a slight increase in the contact angle of the blended films when SOR and SUC was added to the film as compared to the control film. However, the films show contact angle values below 90° , indicating hydrophilicity of the PVA/CW films incorporated with SOR and SUC. Therefore, it can be said that if the contact angle is lower, the degree of solubility is higher.

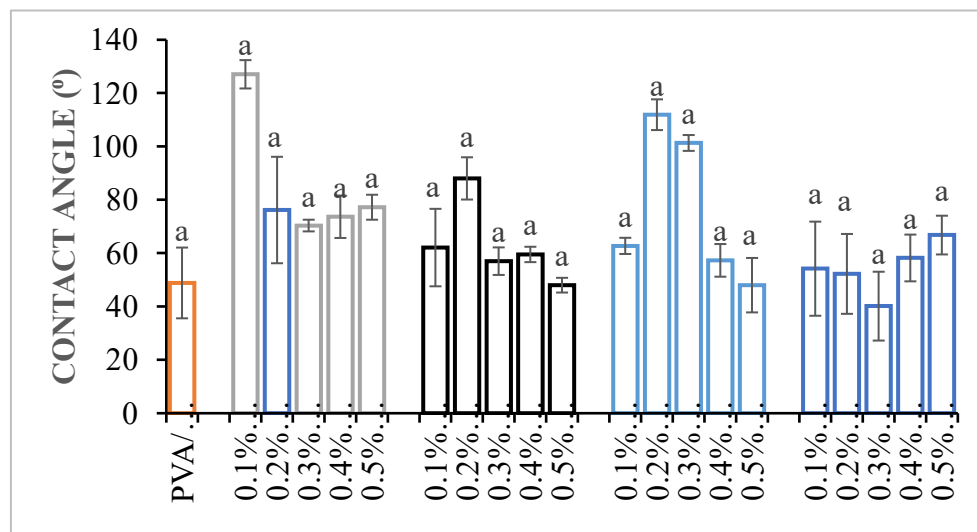


Figure 7. Contact angle of PVA/CW films with different plasticizers. Values represent mean $\pm$ SD. Bar letters (a) indicate that the treatment means are not significantly ($p > 0.05$) different (Table S2).

Overall, the 0.1% GLY and 0.2% GLU show plasticizer types and concentrations suitable for applications requiring water-resistant films. Also, increasing plasticizer concentration generally enhances hydrophilicity but the extent of this effect depends on the plasticizer type.

3.6. Film Solubility

Film solubility in water is an essential property in selecting suitable packaging plastics. For most food applications, films with good hydrophobicity are required to provide water resistance and boost shelf-life of food products [14,38,39]. Plasticization of PVA/CW films and the solubility (%) of these films in water showed a high level of inconsistency. This could be attributed to the hydrophilic nature of plasticizers (particularly polyols) that perform essential role in weakening the interaction between polymer molecular chains, increasing the free space volumes between the chains. This in turn promotes water diffusion into film matrix and, consequently, increases the solubility of plasticized films.

3.7. Mechanical Properties

The mechanical properties of PVA/CW films differ slightly with the type and concentration of plasticizers. Two-way ANOVA revealed no significant effect of plasticizer type ($p = 0.406$), concentration ($p = 0.512$) on tensile strength (TS), and elongation-at-break (EB) as presented in Figure 8a, b. The PVA/CW has a TS of 0.73 MPa and EB of 0.62%. 0.2% SUC film had the highest TS of 3.03 MPa, but TS decreases to 0.55 MPa and 0.47 MPa for 0.4% SUC and 0.5% SUC, respectively. Similarly, GLU plasticized films exhibit TS of 1.08 MPa and 1.47 MPa at 0.1% and 0.2% concentration respectively higher than the unplasticized

film. However, increasing GLU and SUC concentrations (0.4% above) led to visible phase discontinuities and structural heterogeneity in SEM, coinciding with sharp reductions in TS to 0.71 MPa and 0.47 MPa for 0.5% GLU and 0.5% SUC, respectively. The observed increase in TS of GLU and SUC at low concentrations indicate that large saccharide molecules act more like structural modifiers that reinforce intermolecular interactions and chain slippage than a strong plasticizer. Also, the presence of multiple hydroxyl groups promotes extensive hydrogen bonding with PVA, producing a more cohesive matrix capable of efficient stress transfer.

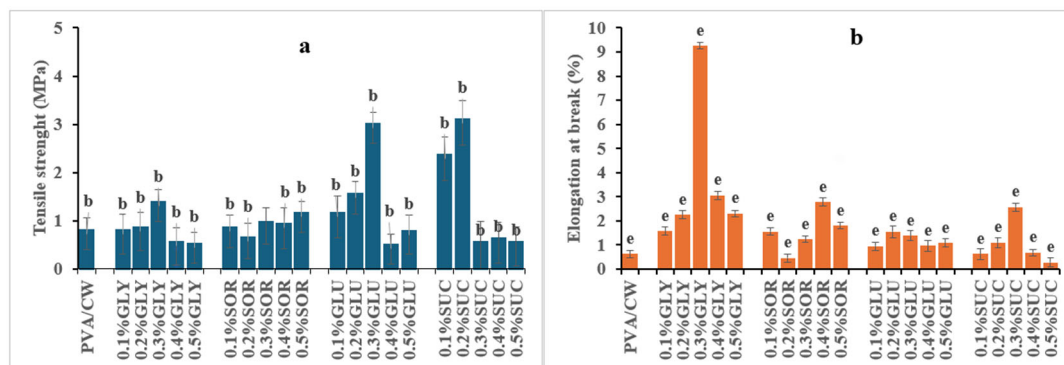


Figure 8. Mechanical properties of PVA/CW films with various plasticizers (a) tensile strength; (b) elongation at break. Values reported are the means $\pm$ standard deviations. Bars with the same letter are not significantly different ($p > 0.05$) (Tables S3 and S4).

Similarly, GLY plasticized films showed a slight increase in TS as concentration increased with the highest TS and EB of 1.31 MPa and 9.26% at 0.3% GLY, respectively. A further increase in GLY beyond 0.3% concentration resulted in decreased TS and EB compared to unplasticized PVA/CW films. In contrast, films plasticized with 0.4% SOR had %EB 2.78% and an intermediate TS of 0.85 MPa compared to other concentrations. This indicates that sorbitol provides better structural integrity while still improving flexibility at moderate concentrations. A study investigated the effect of two plasticizers (glycerol and sorbitol) on the mechanical properties of alginate-based films. They explained that both plasticizers showed a plasticizing effect on alginate-based films by decreasing the tensile strength and increasing the elongation at break. However, it was reported that 30% glycerol was as effective as the incorporation of 50% sorbitol. This was attributed to the low molecular weight of glycerol, which is almost half that of sorbitol [13,18].

Overall, these findings indicate that small plasticizers such as GLY primarily enhance ductility, whereas larger sugars such as GLU and SUC promote structural reinforcement, with SOR having intermediate elongation between polyol and sugar alcohol. Consequently, optimal plasticizer selection should be guided by the intended application, with 0.4% GLY and 0.5% GLY having advantages over other plasticizer types and concentrations in terms of TS and EB.

4. Conclusions

This study achieved its objective of systematically evaluating how plasticizer type and concentration influence the structural, thermal, mechanical, morphological, and surface properties of PVA/CW films. The findings demonstrate that plasticizer chemistry is the dominant factor governing performance by modifying intermolecular interactions, phase distribution, and polymer chain mobility. Importantly, statistical analysis indicated no significant differences among several treatment levels for key response variables, suggesting that within the tested narrow concentration range, performance variations were subtle and application dependent. In general, low molecular weight plasticizers such as GLY at mod-

erate concentrations (0.2–0.4%) provided the better effective improvement in ductility and film homogeneity, making them suitable for applications requiring flexibility and mechanical compliance, such as stretchable agricultural films or secondary packaging. However, at higher concentrations (0.4–0.5%), reductions in tensile strength and increased susceptibility to moisture limit the suitability for load-bearing or high-humidity environments. Similarly, SOR demonstrated comparatively better thermal stability and moderate structural integrity across concentrations, offering advantages for applications requiring dimensional stability and heat resistance; nevertheless, its plasticizing efficiency was lower than GLY, resulting in limited enhancement of elongation. Larger saccharide plasticizers, GLU and SUC, promoted structural cohesion and strength. Morphological observations supported these trends, confirming that uniform phase distribution improved mechanical performance, whereas phase heterogeneity reduced structural efficiency. Film solubility, however, did not follow a consistent trend across formulations, indicating complex interactions among polymer, wax, and plasticizer components. This variability suggests that solubility is controlled by competing mechanisms rather than a single compositional factor. Therefore, further formulation optimization and mechanistic investigation will be conducted in future work to better regulate water sensitivity and enhance functional stability.

In conclusion, future work will focus on expanding the investigated plasticizer concentration range to better identify performance thresholds and transition points in mechanical, thermal, and surface properties. In addition, systematic formulation optimization will be conducted to improve control over film solubility and water sensitivity while maintaining structural integrity. These efforts will enable more precise tailoring of PVA/CW films for specific packaging and agricultural applications.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/polym18050626/s1>, Table S1: Analysis of variance (ANOVA) for thermal stability (°C) of PVA/CW-based films with different treatments; Table S2: Analysis of variance (ANOVA) for contact angle (°) of PVA/CW-based films with different treatments; Table S3: Analysis of variance (ANOVA) for tensile strength (MPa) of PVA/CW-based films with different treatments; Table S4: Analysis of variance (ANOVA) for elongation at break (%) of PVA/CW-based films with different treatments; Table S5: Values of tensile strength (TS), young modulus (YM) and elongation-at-break (EB) for Poly (vinyl) alcohol/Carnauba wax (PVA/CW) films with variation of plasticizer concentrations.

Author Contributions: Conceptualization, A.M.H.; writing—original draft preparation, A.T.T.; methodology, A.M.H. and A.T.T.; writing-review and editing, A.T.T. and A.M.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the North Dakota Corn Council, ND, U.S.; Grant number FAR0036692.

Institutional Review Board Statement: Not applicable.

Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Materials. Further inquiries can be directed to the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Abotbina, W.; Sapuan, S.M.; Sultan, M.T.H.; Alkbir, M.F.M.; Ilyas, R.A. Development and Characterization of Cornstarch-Based Bioplastics Packaging Film Using a Combination of Different Plasticizers. *Polymers* **2021**, *13*, 3487. [\[CrossRef\]](#)
2. Vieira, M.G.A.; Da Silva, M.A.; Dos Santos, L.O.; Beppu, M.M. Natural-based plasticizers and biopolymer films: A review. *Eur. Polym. J.* **2011**, *47*, 254–263. [\[CrossRef\]](#)
3. Donhowe, I.G.; Fennema, O. The effects of plasticizers on crystallinity, permeability, and mechanical properties of methylcellulose films. *J. Food Process. Preserv.* **1993**, *17*, 247–257. [\[CrossRef\]](#)

4. Marta, H.; Indrianti, N.; Aziza, A.J.N.; Sholichah, E.; Budiati, T.; Sarifudin, A.; Cahyana, Y.; Sukri, N.; Pangawikan, A.D. Enhancing Corn Starch-Poly(Vinyl Alcohol) and Glycerol Composite Films with Citric Acid Cross-Linking Mechanism: A Green Approach to High-Performance Packaging Materials. *J. Renew. Mater.* **2026**, *14*, 1. [\[CrossRef\]](#)
5. Tijani, A.T.; Ayodele, T.; Liadi, M.; Sarker, N.C.; Hammed, A. Mechanical and Thermal Characteristics of Films from Glycerol Mixed Emulsified Carnauba Wax/Polyvinyl Alcohol. *Polymers* **2024**, *16*, 3024. [\[CrossRef\]](#)
6. Kovtun, G.; Casas, D.; Cuberes, T. Influence of Glycerol on the Surface Morphology and Crystallinity of Polyvinyl Alcohol Films. *Polymers* **2024**, *16*, 2421. [\[CrossRef\]](#)
7. Caicedo, C.; Díaz-Cruz, C.A.; Jiménez-Regalado, E.J.; Aguirre-Loredo, R.Y. Effect of Plasticizer Content on Mechanical and Water Vapor Permeability of Maize Starch/PVOH/Chitosan Composite Films. *Materials* **2022**, *15*, 1274. [\[CrossRef\]](#) [\[PubMed\]](#)
8. Ballesteros-Mártinez, L.; Pérez-Cervera, C.; Andrade-Pizarro, R. Effect of glycerol and sorbitol concentrations on mechanical, optical, and barrier properties of sweet potato starch film. *NFS J.* **2020**, *20*, 1–9. [\[CrossRef\]](#)
9. Basiak, E.; Lenart, A.; Debeaufort, F. How Glycerol and Water Contents Affect the Structural and Functional Properties of Starch-Based Edible Films. *Polymers* **2018**, *10*, 412. [\[CrossRef\]](#)
10. Carvalho, R.A.; Grosso, C.R.F.; Sobral, P.J.A. Effect of chemical treatment on the mechanical properties, water vapour permeability and sorption isotherms of gelatin-based films. *Packag. Technol. Sci.* **2008**, *21*, 165–169. [\[CrossRef\]](#)
11. Cerqueira, M.A.; Souza, B.W.; Teixeira, J.A.; Vicente, A.A. Effect of glycerol and corn oil on physicochemical properties of polysaccharide films—A comparative study. *Food Hydrocoll.* **2012**, *27*, 175–184. [\[CrossRef\]](#)
12. Hazrati, K.Z.; Sapuan, S.M.; Zuhri, M.Y.M.; Jumaidin, R. Effect of plasticizers on physical, thermal, and tensile properties of thermoplastic films based on *Dioscorea hispida* starch. *Int. J. Biol. Macromol.* **2021**, *185*, 219–228. [\[CrossRef\]](#)
13. Jost, V.; Kobsik, K.; Schmid, M.; Noller, K. Influence of plasticiser on the barrier, mechanical and grease resistance properties of alginate cast films. *Carbohydr. Polym.* **2014**, *110*, 309–319. [\[CrossRef\]](#) [\[PubMed\]](#)
14. McHugh, T.H.; Krochta, J.M. Sorbitol- vs Glycerol-Plasticized Whey Protein Edible Films: Integrated Oxygen Permeability and Tensile Property Evaluation. *J. Agric. Food Chem.* **1994**, *42*, 841–845. [\[CrossRef\]](#)
15. Nordin, N.; Othman, S.H.; Rashid, S.A.; Basha, R.K. Effects of glycerol and thymol on physical, mechanical, and thermal properties of corn starch films. *Food Hydrocoll.* **2020**, *106*, 105884. [\[CrossRef\]](#)
16. Sanyang, M.L.; Sapuan, S.M.; Jawaid, M.; Ishak, M.R.; Sahari, J. Effect of Plasticizer Type and Concentration on Dynamic Mechanical Properties of Sugar Palm Starch-Based Films. *Int. J. Polym. Anal. Charact.* **2015**, *20*, 627–636. [\[CrossRef\]](#)
17. Sanyang, M.L.; Sapuan, S.M.; Jawaid, M.; Ishak, M.R.; Sahari, J. Effect of plasticizer type and concentration on physical properties of biodegradable films based on sugar palm (*Arenga pinnata*) starch for food packaging. *J. Food Sci. Technol.* **2016**, *53*, 326–336. [\[CrossRef\]](#)
18. Tong, Q.; Xiao, Q.; Lim, L.T. Effects of glycerol, sorbitol, xylitol and fructose plasticisers on mechanical and moisture barrier properties of pullulan–alginate–carboxymethylcellulose blend films. *Int. J. Food Sci. Technol.* **2013**, *48*, 870–878. [\[CrossRef\]](#)
19. Parvin, F.; Khan, M.A.; Saadat, A.H.M.; Khan, M.A.H.; Islam, J.M.; Ahmed, M.; Gafur, M.A. Preparation and characterization of gamma irradiated sugar containing starch/poly(vinyl alcohol)-based blend films. *J. Polym. Environ.* **2011**, *19*, 1013–1022. [\[CrossRef\]](#)
20. Stachowiak, N.; Kowalonek, J.; Kozłowska, J. Effect of plasticizer and surfactant on the properties of poly(vinyl alcohol)/chitosan films. *Int. J. Biol. Macromol.* **2020**, *164*, 2100–2107. [\[CrossRef\]](#)
21. ASTM D882-22; Standard Test Method for Tensile Properties of Thin Plastic Sheeting. ASTM International: West Conshohocken, PA, USA, 2022.
22. Lim, R.; Kiew, P.L.; Lam, M.K.; Yeoh, W.M.; Ho, M.Y. Corn starch/PVA bioplastics—The properties and biodegradability study using cultivation. *Asia-Pac. J. Chem. Eng.* **2021**, *16*, e2622. [\[CrossRef\]](#)
23. Chiumarelli, M.; Hubinger, M.D. Evaluation of edible films and coatings formulated with cassava starch, glycerol, carnauba wax and stearic acid. *Food Hydrocoll.* **2014**, *38*, 20–27. [\[CrossRef\]](#)
24. Sothornvit, R.; Krochta, J.M. Plasticizer effect on mechanical properties of β -lactoglobulin films. *J. Food Eng.* **2001**, *50*, 149–155. [\[CrossRef\]](#)
25. Ibrahim, M.I.J.; Sapuan, S.M.; Zainudin, E.S.; Zuhri, M.Y.M. Physical, thermal, morphological, and tensile properties of cornstarch-based films as affected by different plasticizers. *Int. J. Food Prop.* **2019**, *22*, 925–941. [\[CrossRef\]](#)
26. Andrade, J.; González-Martínez, C.; Chiralt, A. The Incorporation of Carvacrol into Poly (vinyl alcohol) Films Encapsulated in Lecithin Liposomes. *Polymers* **2020**, *12*, 497. [\[CrossRef\]](#) [\[PubMed\]](#)
27. Chiumarelli, M.; Hubinger, M.D. Stability, solubility, mechanical and barrier properties of cassava starch—Carnauba wax edible coatings to preserve fresh-cut apples. *Food Hydrocoll.* **2012**, *28*, 59–67. [\[CrossRef\]](#)
28. Gowsia, I.; Mir, F.; Banday, J. Synthesis, characterization, and antimicrobial evaluation of polyvinylalcohol-osthol composite films. *Turk. J. Chem.* **2022**, *46*, 1984–1998. [\[CrossRef\]](#)
29. Musa, B.H.; Hameed, N.J. Study of the mechanical properties of polyvinyl alcohol/starch blends. *Mater. Today Proc.* **2020**, *20*, 439–442. [\[CrossRef\]](#)

30. Muscat, D.; Adhikari, R.; McKnight, S.; Guo, Q.; Adhikari, B. The physicochemical characteristics and hydrophobicity of high amylose starch–glycerol films in the presence of three natural waxes. *J. Food Eng.* **2013**, *119*, 205–219. [[CrossRef](#)]
31. Nasibi, S.; Khoramabadi, H.N.; Arefian, M.; Hojjati, M.; Tajzad, I.; Mokhtarzade, A.; Mazhar, M.; Jamavari, A. A review of Polyvinyl alcohol/Carboxy methyl cellulose (PVA/CMC) composites for various applications. *J. Compos. Compd.* **2020**, *2*, 68–75. [[CrossRef](#)]
32. Sanyang, M.L.; Sapuan, S.M.; Jawaaid, M.; Ishak, M.R.; Sahari, J. Effect of Plasticizer Type and Concentration on Tensile, Thermal and Barrier Properties of Biodegradable Films Based on Sugar Palm (*Arenga pinnata*) Starch. *Polymers* **2015**, *7*, 1106–1124. [[CrossRef](#)]
33. Zhang, Y.; Han, J.H. Mechanical and Thermal Characteristics of Pea Starch Films Plasticized with Monosaccharides and Polyols. *J. Food Sci.* **2006**, *71*, E109–E118. [[CrossRef](#)]
34. Arifin, H.R.; Djali, M.; Nurhadi, B.; Hasim, S.A.; Hilmi, A.; Puspitasari, A.V. Improved properties of corn starch-based bio-nanocomposite film with different types of plasticizers reinforced by nanocrystalline cellulose. *Int. J. Food Prop.* **2022**, *25*, 509–521. [[CrossRef](#)]
35. Azahari, N.A.; Othman, N.; Ismail, H. Biodegradation studies of polyvinyl alcohol/corn starch blend films in solid and solution media. *J. Phys. Sci.* **2011**, *22*, 15–31.
36. Sobral, P.D.A.; Monterrey-q, E.S.; Habitante, A.M.Q.B. Glass Transition Study of Nile Tilapia Myofibrillar Protein Films Plasticized by Glycerin and Water. *J. Therm. Anal. Calorim.* **2002**, *67*, 499–504. [[CrossRef](#)]
37. Edhirej, A.; Sapuan, S.M.; Jawaaid, M.; Zahari, N.I. Effect of various plasticizers and concentration on the physical, thermal, mechanical, and structural properties of cassava-starch-based films. *Starch-Stärke* **2017**, *69*, 1500366. [[CrossRef](#)]
38. Kristo, E.; Biliaderis, C.G. Water sorption and thermo-mechanical properties of water/sorbitol-plasticized composite biopolymer films: Caseinate–pullulan bilayers and blends. *Food Hydrocoll.* **2006**, *20*, 1057–1071. [[CrossRef](#)]
39. Thakore, I.M.; Desai, S.; Sarawade, B.D.; Devi, S. Studies on biodegradability, morphology and thermo-mechanical properties of LDPE/modified starch blends. *Eur. Polym. J.* **2001**, *37*, 151–160. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.