Food Packaging and Shelf Life 51 (2025) 101590

Contents lists available at ScienceDirect

Food Packaging and Shelf Life

journal homepage: www.elsevier.com/locate/fpsl

Investigating the effect of three different types and concentrations of plasticizers on physico-mechanical properties of pullulan food-packaging films

Ghazal Zamanidehyaghoubi, Fakhri Shahidi *, Mohammad Reza Edalatian Dovom *, Mohebbat Mohebbi, Sahar Roshanak

Department of Food Science and Technology, Faculty of Agriculture, Ferdowsi University of Mashhad, Mashhad, Iran

ARTICLE INFO

Keywords:
Biodegradable packaging
Biopolymer
Glycerol
Sorbitol
Fructose

ABSTRACT

This study aimed to evaluate the effect of plasticizer type (glycerol, sorbitol and fructose) and concentration (5, 7.5 and 10 % w/w) on pullulan films' thickness, moisture content (MC), tensile strength (TS), elongation at break (EAB), folding endurance (FE), water vapor permeability (WVP), oxygen permeability (O_2P), oil resistance (OiR), ultra violet and visible light transmittance (Tr_{280} and Tr_{660}), disintegration time (DT), weight loss (WL), microstructure and thermal properties. A 3-factor 3-level full factorial design of experiments was used to develop films through solution casting method. Maximum thickness, MC, EAB, FE, WVP, O_2P, Tr_{280}, Tr_{660}, and WL were achieved using glycerol followed by sorbitol and fructose, while maximum TS, homogeneity and glass transition temperature (Tg) were achieved using fructose followed by sorbitol and glycerol at same concentrations. Increasing plasticizers' concentration from 5 % to 10 % w/w resulted in the reduction of TS, homogeneity and Tg, and elevation of thickness, EAB, FE, MC, WVP, O_2P, Tr_{280}, Tr_{660} and WL ($p < 0.05$). Neither the type nor the concentration of plasticizer affected OiR and DT significantly. Sorbitol at 7.5 % w/w was the most suitable choice for producing pullulan-based films with oil impermeability, homogeneity, Tg of 208 °C, high TS (29.83 ± 1.01 MPa), EAB (18.32 % ± 0.32), FE (37 ± 3), Tr_{660} (58.04 % ± 1.21) and WL (45.44 % ± 0.43), and low DT (51.36 ± 0.05 s), MC (18.13 % ± 0.26), WVP (1.18 ± 0.13 (g/m.s.Pa)× 10^{-10}), O_2P (peroxide value (PV) = 14.86 ± 0.15 meq/kg), Tr_{280} (37.19 % ± 0.14) and thickness (0.043 ± 0.009 mm).

1. Introduction

Food industries face challenges in reducing waste in supply chain. Food packaging films can be important tools in reducing food wastes (Wu et al., 2024). Synthetic plastics are extensively used in food packaging due to their stability, affordability, high tensile strength (TS) and good barrier properties (Moradi et al., 2019; Xin et al., 2020). However, plastics cause environmental repercussions, posing hazards for plants, animals and humans (Agrawal et al., 2021; Islam et al., 2020; Rostami and Esfahani, 2019). The demand of consumer market for biopolymer-based packaging films is increasing due to their biodegradability and eco-friendly properties (Liu et al., 2019; Wang et al., 2019; Wu et al., 2023). Pullulan $(C_6H_{10}O_5)_n$ is an edible, water-soluble and high molecular weight biopolymer produced by *Aureobasidium pullulans* that is gaining significant interest due to its desirable film forming properties (Silva et al., 2018). This neutral exopolysaccharide is mainly composed of maltotriose as the repeating unit polymerized in a linear fashion. Homopolysaccharide pullulan shows stable aqueous solutions across a wide pH range and inhibition against fungal growth (Hassan and Cutter, 2020; Tabasum et al., 2018). Pullulan-based films are biocompatible, colorless, odorless, tasteless, transparent, heat-sealable, thermally stable and impermeable to oil, while showing water and gas permeability, high sensitivity to humidity, and weak mechanical properties, which restrict their exploitation (Liu et al., 2019; Rostami and Esfahani, 2019). Plasticization process is a viable method to optimize such properties for commercial applications (El Miri et al., 2018; Farhan and Hani, 2017).

Plasticizers, as nonvolatile liquids or low melting solids, are characterized by their colorless, odorless, high boiling point, low molecular weight and non-separating properties. They exhibit high compatibility

* Corresponding authors.
E-mail addresses: ghazalzamani@mail.um.ac.ir (G. Zamanidehyaghoubi), fshahidi@um.ac.ir (F. Shahidi), edalatian@um.ac.ir (M.R. Edalatian Dovom), m-mohebbi@um.ac.ir (M. Mohebbi), s.roshanak@um.ac.ir (S. Roshanak).

https://doi.org/10.1016/j.fpsl.2025.101590
Received 22 February 2025; Received in revised form 30 June 2025; Accepted 2 August 2025
Available online 6 August 2025

with the film-forming polymers and improve their brittleness, hardness, flexibility, workability, processability and handling properties when added in optimal quantities (El Miri et al., 2018; Mukuze et al., 2019; Vuddanda et al., 2017). The concentration and chemical composition of these essential components in the films, have a significant impact on film formation and its final properties (El Miri et al., 2018; Farhan and Hani, 2017). Glycerol, sorbitol and fructose are FDA-approved food additives and the most popular cost-effective plasticizers. Glycerol, with molecular formula of $C_3H_8O_3$ and molecular weight of 92.094 g/mol, is a water-soluble polyol mostly used in hydrocolloid films (González-Torres et al., 2021; Mukuze et al., 2019). Sorbitol, having $C_6H_{14}O_6$ molecular formula and 182.17 g/mol molecular weight, is beneficial for plasticizing polymers rich in -OH or -NH, but resists water because of weaker water affinity and stronger polymer interaction (González-Torres et al., 2021; Tian et al., 2017). Unlike glucose, fructose has a ketonic carbonyl group instead of an aldehydic one. Fructose, with molecular formula of $C_6H_{12}O_6$ and molecular weight of 180.156 g/mol, has been used as a plasticizer in the literature (Mukuze et al., 2019).

Several studies have focused on the effects of glycerol, sorbitol or fructose on the properties of cellulose nanocrystals filled alginate (El Miri et al., 2018), semi-refined kappa-carrageenan (Farhan & Hani, 2017), potato starch (González-Torres et al., 2021; Islam et al., 2020), cassava bioplastic (Mukuze et al., 2019), pea starch (Saberi et al., 2016) and polyvinyl alcohol (Tian et al., 2017) films. Nevertheless, to the best of our knowledge, the effects of these plasticizers on pure pullulan packaging films have not yet been investigated in the literature. In view of this, this study aimed to assess the effect of glycerol, sorbitol and fructose at different concentrations on pullulan films' physico-mechanical characteristics.

2. Materials and methods

2.1. Materials and chemicals

Food grade pullulan ($\geq$ 95 %) was provided from Shaanxi Huatai Bio-Fine Chemical Co., Ltd, China. Analytical grade glycerol, sorbitol, fructose, etc. were supplied by Merck Chemical Co. (Darmstadt, Germany). Deionized water was used throughout the work and all chemicals were utilized without further purification.

2.2. Film preparation using experimental design

Pullulan films were developed using casting method (Vuddanda et al., 2017). According to a 3-factor, 3-level full factorial (3^2) design of experiments (Table 1), pullulan and plasticizers (glycerol, sorbitol and fructose) at different ratios of 5, 7.5 and 10 % w/w (with respect to pullulan weight), were magnetically stirred in water for 1 h at 800 rpm. The solutions were filtered and left for 1 h to remove air bubbles before being cast on levelled glass plates. Films' thickness was mostly controlled through keeping the suspension amount constant. The resulting films were air-dried at ambient conditions for 12 h and then peeled off from the plates. The standardization was conducted by pre-conditioning the films in a desiccator with 50 % relative humidity (RH) and 25 °C temperature for 48 h before testing. The experimental range of the plasticizer concentration was pre-determined through batch experiments, making discussion on extreme values of the factors unnecessary. For example, the films were analyzed visually and tactilely to examine their uniformity (absence of bubbles and cracks) and ease of handling. Plasticizer concentrations $<$ 5 % w/w were insufficient to plasticize the films as they formed brittle films, while adding plasticizers at $>$ 10 % w/w caused issues in drying the films, resulting in sticky films that were challenging to handle and remove from plates. The tackiness observed with these films may indicate either plasticizer phase separation or excessive plasticizer diffusing to the surface after sufficient interacting with pullulan chains (Vuddanda et al., 2017).

Table 1
Film formulations based on the full factorial (3^2) design of experiments.

Formulation code	Experimental factors	
	Plasticizer type	Plasticizer concentration (%w/w)
1: PG_5	Glycerol	5
2: $PG_{7.5}$	Glycerol	7.5
3: PG_{10}	Glycerol	10
4: PS_5	Sorbitol	5
5: $PS_{7.5}$	Sorbitol	7.5
6: PS_{10}	Sorbitol	10
7: PF_5	Fructose	5
8: $PF_{7.5}$	Fructose	7.5
9: PF_{10}	Fructose	10
Control	-	0

2.3. Film characterization

2.3.1. Thickness

A hand-held digital micrometer (Mitutoyo Corporation, Kanagawa, Japan) with 0.001 mm precision was used to measure the films' thickness. Measurements were taken at three random locations on each film and the average of the readings was reported.

2.3.2. Moisture content (MC)

MC was determined by measuring the mass loss of the films after heating at 105 °C for 24 h (until reaching a constant weight) (Rostami & Esfahani, 2019).

2.3.3. Mechanical properties

TS and elongation at break (EAB) of the films were evaluated with a texture analyzer (TexturePro CT V1.5 Build, Brookfield Engineering Labs. Inc.) under controlled conditions at 25 °C. The machine's clamps held 1.5 cm on each end of the rectangular film strip (8 × 1.5 cm), leaving an effective testing area of 5 × 1.5 cm^2. The film was stretched vertically by the upper clamp at a cross-head speed of 50 $mm.min^{-1}$ until it ruptured. Ultimately, TS and EB were calculated using Eqs. (1) and (2), respectively.

$$TS(MPa) = \frac{Fmax}{A} \quad (1)$$

$$EAB(\%) = \frac{\Delta L}{L0} \times 100 \quad (2)$$

where F_{max}, A, ΔL and L_0 represented the maximum force required to break the film (N), film's cross-sectional area (m^2), increase in film length at the point of rupture (m), and initial length of the film (50 mm), respectively (Roy & Rhim, 2020).

Folding endurance (FE) of the films was determined by manually measuring the number of times a film strip could be folded at 180° in the same place without breaking or forming visible cracks (Galgatte et al., 2013).

2.3.4. Barrier properties

2.3.4.1. Water vapor permeability (WVP). The films' WVP was determined using the method of Gheribi et al. (2023), with slight modification (Gheribi et al., 2023). The glass bottles, with 20 mm diameter, were filled with either 4 g of anhydrous $CaCl_2$ desiccant (0 % RH) or nothing (control), sealed tightly with film pieces, weighed and placed in a desiccator at 25 °C with a 75 % RH gradient. The determination of water vapor transport involved recording the bottle's weight gain during a steady state transfer, with measurements taken each hour for a duration of 8 h. The weight changes were plotted over time and linear regression was used to calculate slopes. The water vapor transmission rate (WVTR) was then calculated by dividing the straight line's slope (g/s) by the bottle mouth's area (m^2). Finally, the WVP ((g/m.s.Pa) × 10^{-10}) was

calculated using Eq. (3):

$$WVP = WVTR\frac{X}{\Delta P} \rightarrow WVP = \frac{\Delta m}{A\Delta t}\frac{X}{\Delta P} \quad (3)$$

where $\Delta m/\Delta t$, A, X and ΔP implied the weight of moisture gain per unit time (g/s), exposed film surface area (m^2), film thickness (m) and difference in water vapor pressure between the film's outside and inside (Pa), respectively (Thakur et al., 2017).

2.3.4.2. Oxygen permeability (O_2P). The films' O_2P was determined using a modified version of the technique described by Akman et al. (2021), Akman et al. (2021). Film specimens were used to cover 25 mL conical flasks holding 15 mL of antioxidant-free sunflower oil and were then stored in an oven at 60 °C for 9 days. The change of peroxide value (PV) in oil samples was measured using sodium thiosulfate titration technique. One control sample lacked film covering.

2.3.4.3. Oil resistance (OiR). 3 g soybean oil was added to a glass test tube, followed by sealing the open end of glass tube with a 50 × 50 mm film strip. Afterward, the tube was upside down, placed on a filter paper supported by a glass slide and kept in a desiccator at 25 °C and 75 % RH. The gained weight of the filter paper after 3 days was reported as OiR (%) (Chen et al., 2014).

2.3.4.4. Light barrier properties. The films' optical characteristics were assessed spectrophotometrically (Sigma, 30–3 k UV–Vis spectrophotometer) by measuring ultra violet and visible light transmittance (Tr_{280} and Tr_{660}) through the films at 280 nm and 660 nm, respectively. The empty test cuvette was considered as blank (Kanmani & Rhim, 2014).

2.3.5. Degradation assay

2.3.5.1. Film disintegration. The disintegration time (DT) of the films was determined using the petri dish method (Pezik et al., 2021).

2.3.5.2. Biodegradability. Soil degradation experiments were performed using weight measurements of the film samples before and after burial in soil, under natural environmental conditions (Li et al., 2020).

2.3.6. Microstructure

A Scanning Electron Microscope (SEM, Model VP 1450, LEO Co., Germany) operating at 20.00 kV was used to study the surface and cross-sectional morphology of the films. The cryo-fractured films in liquid nitrogen were sputter-coated with gold before obtaining the micrographs (Vuddanda et al., 2017).

2.3.7. Thermal properties

A Differential Scanning Calorimeter (DSC, METTLER TOLEDO, Model 822e, Switzerland) was used to determine the films' thermal properties over a temperature range of 0–240 °C at a heating rate of 10 °C/min under N_2 gas. Dried film disks (~ 5 mg) at 150 °C were weighed in aluminum DSC pans and hermetically sealed. An empty pan served as reference.

2.4. Statistics

The Minitab statistical analysis software (v17.0 for windows) was used for the design of experiments and all subsequent statistical analyses. The measurements were carried out in triplicate and the results were presented as means ± standard deviations (S.D). The experimental data was analyzed by ANOVA and the statistical significance of samples through mean comparisons were conducted using Tukey's test at a 95 % confidence level ($p < 0.05$).

3. Results and Discussion

3.1. Thickness

The film thickness depends on film composition and plays a crucial role in determining physical and barrier properties (Moradi et al., 2019; Rostami and Esfahani, 2019). Film thickness has a significant impact on packaging system functionality and drying kinetics, thus controlling this parameter is essential. Film thickness is usually between 0.012 and 0.1 mm (Pezik et al., 2021; Thakur et al., 2017). As shown in Fig. 1.a, thickness values ranged from 0.015 ± 0.003–0.069 ± 0.002 mm. As the plasticizer concentration increased from 5 % to 10 % w/w, the thickness of the films plasticized with glycerol, sorbitol and fructose increased significantly ($p < 0.05$) from 0.023 ± 0.005, 0.019 ± 0.007 and 0.015 ± 0.003–0.069 ± 0.002, 0.064 ± 0.003 and 0.06 ± 0.005 mm, respectively, due to the increased total mass of the films and increased interstitial spacing between polymer chains (Saberi et al., 2016). In contrast, PG_5, PS_5 and PF_5 showed slightly lower thickness values than the unplasticized (control) film (0.025 ± 0.008 mm) ($p > 0.05$). This was probably due to the antiplasticization effect of plasticizers at 5 % w/w, caused by strong polymer-plasticizer interactions via H-bonding, leading to reduction in free volume and thickness. Notably, the plasticizer type did not significantly affect the film thickness ($p > 0.05$). Some previous studies have also documented this correlation of plasticizers with film thickness (Farhan and Hani, 2017; Pezik et al., 2021; Thakur et al., 2017).

3.2. MC

The physico-mechanical and barrier properties of the films depend on MC due to the plasticizing effect of water (Akman et al., 2021; Thakur et al., 2017). Therefore, film's MC is a substantial parameter influencing the packaged food quality (Pezik et al., 2021; Rostami and Esfahani, 2019). The film's MC is influenced by the composition of materials, including both the polymer matrices and plasticizers. The H-bond interactions between polymer chains can decrease -OH group availability and interactions with water, but pullulan's hydrophilic nature aids in moisture retention in films. On the other hand, plasticizers' hydrophilicity can indirectly raise MC by increasing water absorption. Therefore, glycerol, sorbitol and fructose chemically retain moisture, preventing evaporation. As depicted in Fig. 1.b, MC increased with increasing plasticizer concentration from 5 up to 10 % w/w ($p < 0.05$) probably due to the hydrophilic nature of the plasticizers, which facilitates H-bonding with free -OH groups in water molecules. The MC increased significantly from 14.01 % ± 0.19–39.97 % ± 0.31 by elevating glycerol proportion from 5 % to 10 % w/w. Correspondingly, for films plasticized with sorbitol and fructose, MC increased prominently from 11.91 % ± 0.13 and 11.12 % ± 0.06–26.02 % ± 0.04 and 15.82 % ± 1.17, respectively. Therefore, there was a significant distinction in the MC of glycerol-, sorbitol- and fructose- plasticized films probably due to the different molecular weight, molecular structure and hydrophilicity of the plasticizers. The small molecule glycerol can be inserted between pullulan chains to disrupt polymer–polymer H-bonds more easily than larger plasticizer molecules like sorbitol and fructose. Furthermore, the higher hydrophilicity level of glycerol may be the other reason for increased water retention at the end of film drying. Sorbitol and fructose have almost similar molecular weights, but sorbitol-plasticized films showed higher MC than fructose-plasticized films probably due to the fructose's stronger interfacial interactions with pullulan through H-bonding, resulting in fewer -OH groups in the fructose-plasticized films. Notably, films with 5 % w/w plasticizer exhibited lower MC than control film (14.29 % ± 0.09) probably due to antiplasticizer function of the plasticizers. Plasticizers at 5 % w/w can interact strongly with polymer molecules, leading to steric hindrance and fewer available active sites for water absorption. Comparable findings have been documented regarding the impact of plasticizers on the MC of

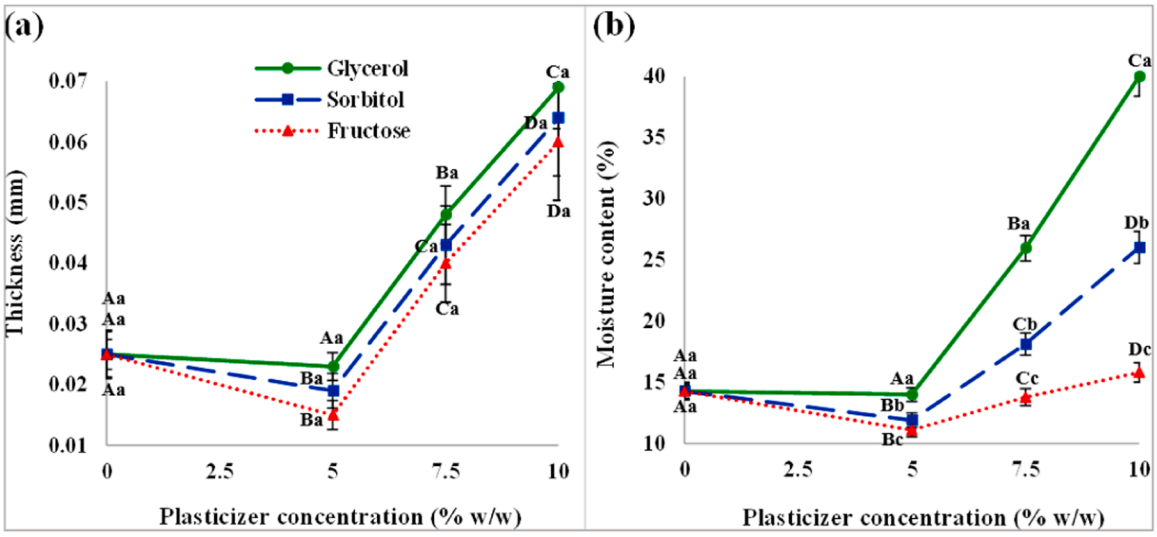

Fig. 1. Thickness (a) and Moisture content (b) of pullulan-based films as affected by plasticizer types and concentrations; Mean values with different uppercase letters in the same plasticizer type and lowercase letters at the same plasticizer concentration are significantly different ($p < 0.05$).

hydrocolloid films (Li et al., 2020; Memiş et al., 2017).

3.3. Mechanical analysis

TS evaluates film strength, whereas EAB determines film's extensional capacity prior to rupture. Packaging films must possess high mechanical strength and flexibility without brittleness, reflected by high TS and EAB (Liu et al., 2019; Monjazeb Marvdashti et al., 2019; Shah et al., 2020). It was observed that exceeding 10 % w/w plasticizer concentration led to film's structural weakness and instability and prevented mechanical measurements, highlighting the crucial role of plasticizer quantity in creating films with desirable mechanical characteristics. On the other hand, as observed in Fig. 2.a&b, control films exhibited a high TS of 30.42 ± 0.93 MPa, but they were prone to cracking when handled due to their low EAB (16.03 % ± 0.09). Consequently, plasticizer addition was considered necessary for film formation. With increasing plasticizer concentration from 0 % to 5 % w/w, TS increased and EAB decreased probably due to the anti-plasticization effect caused by the association of plasticizer molecules with pullulan hydrophilic side groups. Antiplasticization effect can lead to a decrease in free volume in the polymer matrix and suppress polymer chain motion, hindering secondary relaxation mechanisms. In contrast, TS decreased and EAB increased significantly as plasticizer concentration increased from 5 % to 10 % w/w ($p < 0.05$). This was probably due to the microstructural changes, movement and rearrangements of the macromolecule chains caused by reversal of the antiplasticization effect

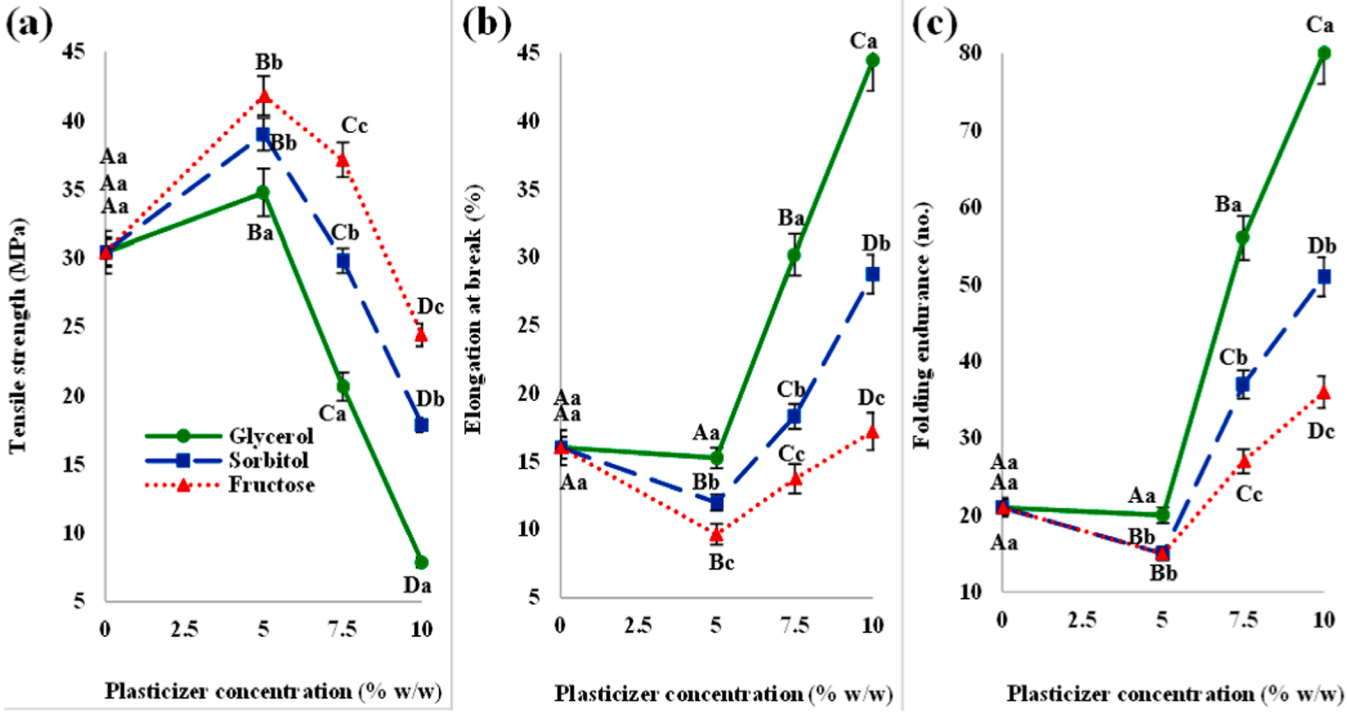

Fig. 2. Tensile strength (a), elongation at break (b) and folding endurance (b) of pullulan films as affected by plasticizer types and concentrations; Mean values with different uppercase letters in the same plasticizer type and lowercase letters at the same plasticizer concentration are significantly different ($p < 0.05$).

to the plasticization effect above the antiplasticization regime (plasticizer concentrations > 5 % w/w), at which plasticizers soften the pullulan's structure and increase its stretchability and mobility, but weaken its rigidity, cohesiveness and chain-chain interactions by lowering its strong intra- and intermolecular H-bonding. Additionally, thickness plays a vital role in TS calculation. Thus, the reduction in TS at plasticizer concentrations > 5 % w/w can also be due to the rise in film thickness (A) in the TS Eq. ($TS = F_{max}/A$). Adding plasticizers changed the films' TS and EAB to different extents depending on the plasticizer type used. By increasing glycerol proportion from 5 % to 10 % w/w, TS of the films plasticized with glycerol, sorbitol and fructose decreased significantly from 34.73 ± 0.55, 38.97 ± 0.48 and 41.79 ± 0.28–7.86 ± 0.32, 17.86 ± 0.71 and 24.43 ± 0.75 MPa, respectively. In contrast, the EAB of the glycerol-, sorbitol- and fructose- plasticized films increased significantly from 15.26 % ± 0.27, 11.98 % ± 0.23 and 9.65 % ± 0.44–44.42 % ± 1.85, 28.76 % ± 1.54 and 17.21 % ± 0.18, respectively, as plasticizer concentration increased from 5 % to 10 % w/w. Our findings revealed that glycerol yields more flexible and less rigid films than other plasticizers, so it is most effective in plasticizing pullulan films. This can be attributed to the higher MC levels in glycerol-plasticized films. Glycerol's hydrophilic nature enables it to hold a greater number of H_2O molecules, which cause extra plasticizing effect and exert a direct influence on the mechanical properties. Moreover, the plasticizers' structure, composition, size, shape and compatibility with polymer matrices affect their performance in film networks and how they interact with polymer networks. For example, sorbitol and fructose have more -OH groups and create more H-bonds with pullulan matrix, resulting in a denser and less flexible network. Furthermore, sorbitol and fructose have longer molecular chains between OH and carbon atoms, leading to a stronger combination with pullulan through H-bonds, thereby increasing film TS. The lower molecular weight of glycerol compared to sorbitol and fructose results in poorer mechanical properties of the pullulan-glycerol films. Eventually, as depicted in Fig. 2.c, FE followed a similar trend as the EAB data. The current findings agreed with many previous studies (El Miri et al., 2018; Farhan and Hani, 2017; Islam et al., 2020; Pezik et al., 2021; Thakur et al., 2017; Zhou et al., 2023).

3.4. Barrier properties

Film permeability is influenced by its thickness, morphology and chemical structure, permeant nature and environment RH and temperature (Akman et al., 2021). The resistance of films against fluid penetration is crucial for package integrity, preventing food interaction with gasses and liquids and limiting microbial growth inside the package (Mihaly-Cozmuta et al., 2017; Monjazeb Marvdashti et al., 2019; Yang et al., 2020). The evaluation of moisture transport between food and the environment is accomplished through the WVP (Rostami and Esfahani, 2019; Thakur et al., 2017; Wu et al., 2019). WVP is affected by the film's water activity and natural properties of the film components (Wu et al., 2019; Wu et al., 2019), and should be as low as possible to prevent moisture loss from the fresh produce (El Miri et al., 2018). As indicated in Fig. 3.a, WVP followed a similar trend as the EAB data. The absence of side chains in pullulan molecular chain led to a close arrangement of molecular chains in control film, making it challenging for water molecules to permeate ($WVP = 0.82 \pm 0.04$ (g/m.s.Pa)$\times 10^{-10}$). On the other hand, pullulan and plasticizer binding in the antiplasticization region created a crosslinking network in the film structure and slowed down the permeability rate, resulting in the lowest WVP values of 0.76 ± 0.05, 0.51 ± 0.04 and 0.29 ± 0.06 (g/m.s.Pa)$\times 10^{-10}$ for pullulan films plasticized with 5 % w/w glycerol, sorbitol and fructose, respectively. Above the antiplasticization region, however, films' WVP increased significantly ($p < 0.05$) probably due to the structural modifications and polysaccharidic network reorganization, resulting in higher free volume, segmental motions, water molecules' diffusion and higher WVP. Plasticizers interact easily with biopolymer chains by decreasing internal H-bonding and increasing mobility, intermolecular spacing and water clustering on the polymer, leading to higher permeability of the films. Another parameter affecting WVP and O_2P is the thickness. Thus, the increase in WVP at higher plasticizer ratios could be

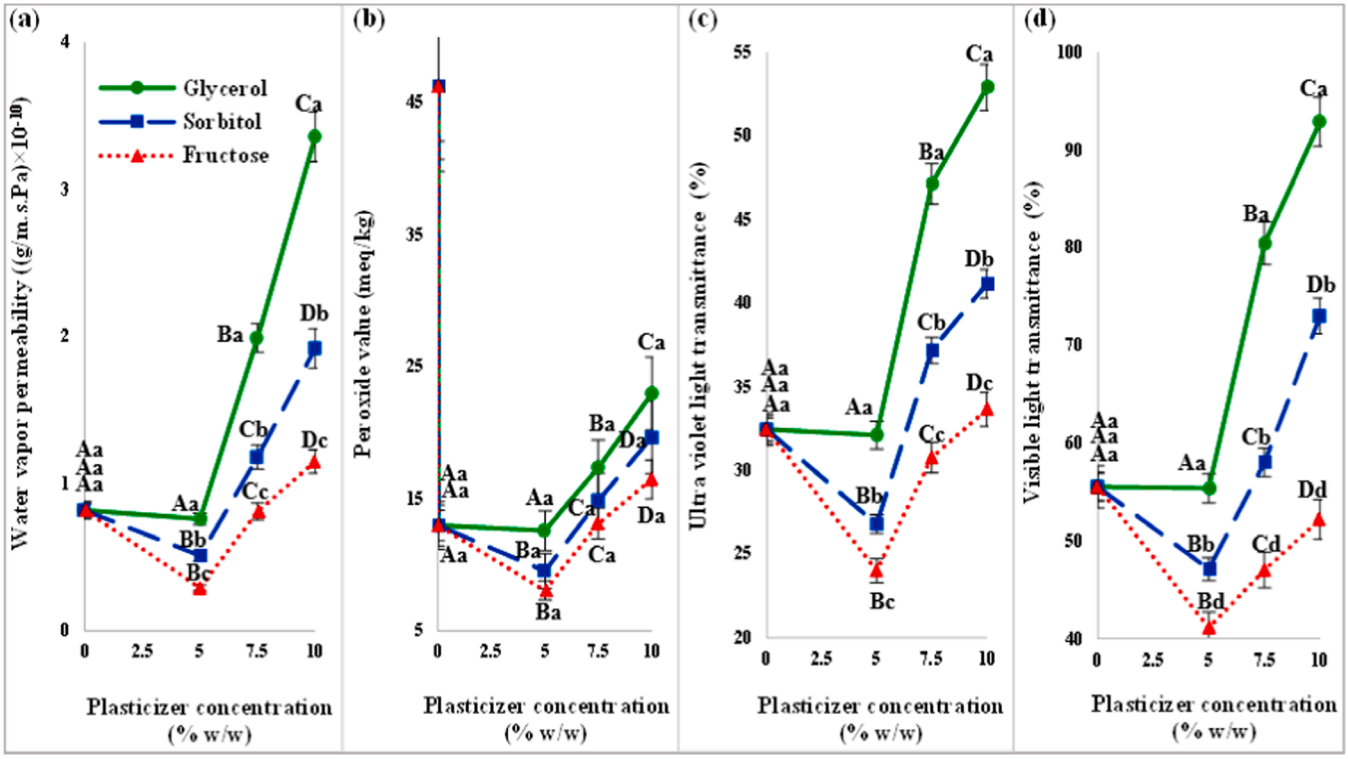

Fig. 3. Effect of plasticizers on water vapor permeability (a), peroxide value (b), ultra violet light transmittance (c) and visible light transmittance (d); Mean values with different uppercase letters in the same plasticizer type and lowercase letters at the same plasticizer concentration are significantly different ($p < 0.05$).

also explained by increase in film thickness (X) in the WVP Eq. (WVP = WVTR × X/ΔP). On the other hand, the hydrophilic nature, hygroscopicity level and chemical structure of the plasticizers remarkedly affected the films' moisture barrier property. Specifically, as the plasticizer concentration increased to 10 % w/w, WVP of the glycerol-, sorbitol- and fructose- plasticized films increased significantly to 3.36 ± 0.21, 1.92 ± 0.07 and 1.15 ± 0.14 (g/m.s.Pa)× 10^{-10}, respectively. Our findings were in accordance with the previously recorded results (El Miri et al., 2018; Farhan and Hani, 2017; Rostami and Esfahani, 2019; Thakur et al., 2017).

O_2P of the films is frequently evaluated due to the negative impact of lipid and food ingredient oxidation on food quality. The film's oxygen barrier ability decreases with increasing O_2P (Kurt & Kahyaoglu, 2014). As indicated in Fig. 3.b, all films reduced oil oxidation significantly ($p < 0.05$). Higher PV means higher O_2P. PV was the highest for uncovered oil (46.27 ± 0.22 meq/kg) due to direct exposure to external oxygen, however, PV of the oil covered with the films varied between 8.04 ± 0.04 and 22.98 ± 0.15 meq/kg. Both O_2P and WVP of the films followed a comparable pattern and the aforementioned explanations about the dependence of WVP on plasticizer concentration are equally applicable to O_2P. Notably, the plasticizer type did not significantly affect the film O_2P ($p > 0.05$). Many previous studies have observed similar behaviors, and the differences in reported PVs could be due to differences in storage time, initial PV of the oil, and the oxygen-blocking quality of the film matrices (Farhan and Hani, 2017; Gounga et al., 2007).

To delve deeper into the practical use of pullulan films in packaging, an investigation was conducted to evaluate the permeability of the films against soybean oil. Pullulan films must exhibit anti-permeability towards oil to prevent possible leakage and maintain appearance, flavor, and properties of enclosed oily or liquid oil-containing articles. Our results showed that the oil did not penetrate any of the films probably due to the hydrophobic resistance of pullulan and plasticizers, which prevent oil molecules from adhering to the film surface. The hydrophobic resistance of the films can be attributed to several key factors: (I) Hydrophilic or oleophobic nature of pullulan and plasticizers; Several studies have suggested that -OH functional groups influence the interaction between polar and non-polar substances, affecting oil repellency. Pullulan is a polysaccharide with a high density of -OH groups, which strongly interact with water molecules but exhibit low affinity for non-polar substances like oils. This hydrophilic nature prevents oil penetration by forming a barrier against non-polar compounds. (II) Plasticizer influence on film structure; Glycerol and sorbitol act as plasticizers, modifying the film's flexibility and moisture retention properties. Their -OH groups contribute to H-bonding, reinforcing the hydrophilic matrix and further reducing oil absorption. Fructose, being a sugar-based plasticizer, enhances film cohesion and reduces porosity, limiting oil diffusion through the matrix. (III) Water-oil barrier properties; The high water-affinity of pullulan-based films creates a moisture-rich environment, which competes with oil molecules for interaction sites. This preference for water absorption over oil absorption enhances the film's OiR (Lakhawat et al., 2023; Tong et al., 2013; Zhou et al., 2023). Hence, pullulan-based films, with or without plasticizer, demonstrate promising OiR and could serve as eco-friendly packaging materials for oily or liquid oil containing articles. Similar results have been reported previously (Lu et al., 2022; Wu et al., 2019).

Films' optical characteristics are important for packaging as they greatly affect consumers' willingness to purchase. UV blockage is necessary to prevent unwanted photocatalytic reactions and color changes, while high transparency (Tr_{660}) allows for clear viewing of packaged foods (Roy and Rhim, 2020; Wang et al., 2019). However, low transparency packaging films safeguard food items sensitive to light against photodegradation. Transparency and opacity have an inverse association. Films with high internal transmittance are transparent, but those with low internal transmittance are opaque (Biao et al., 2019; Monjazeb Marvdashti et al., 2019). The light transmittance through pullulan films was measured at wavelengths of 280 and 660 nm to evaluate their optical properties (Fig. 3.c&d). Increasing plasticizer concentration from 5 % to 10 % w/w resulted in the films with higher T_{660} and T_{280} values ($p < 0.05$) probably due to the enhanced mobility and intermolecular spacing in the pullulan network, making it easier for light to pass through the films. However, PG_5, PS_5 and PF_5 exhibited lower T_{660} (55.54 % ± 0.23) and T_{280} (32.46 % ± 0.08) than those of the control film probably due to changes in the network structure caused by the interaction between pullulan and plasticizer. The -OH groups of plasticizers at 5 % w/w caused a denser and more compact structure, resulting in a modified refractive index that limited light transmission through the films. Further, the glycerol-plasticized films showed higher light transmittance compared to the sorbitol- and fructose- plasticized films ($p < 0.05$). The aforementioned explanations about the dependence of WVP on plasticizer type are equally applicable to T_{660} and T_{280}. Specifically, the film's T_{280} increased significantly from 32.12 % ± 0.95–52.93 % ± 0.06 by increasing glycerol proportion from 5 % to 10 % w/w. Correspondingly, for films with sorbitol and fructose, T_{280} increased remarkedly from 26.78 % ± 0.27 and 24.01 % ± 0.36–41.17 % ± 0.73 and 33.65 % ± 0.11, respectively. Moreover, the T_{660} of the glycerol-, sorbitol- and fructose- plasticized films increased significantly from 55.38 % ± 0.45, 47.11 % ± 0.22 and 41.13 % ± 0.39–92.88 % ± 0.43, 73.02 % ± 0.77 and 52.21 % ± 0.76, respectively, as plasticizer concentration increased from 5 % to 10 % w/w. These results were in line with a study, which reported that higher plasticizer concentration results in lower opacity (Farhan & Hani, 2017).

3.5. Degradation tests

Water solubility, as a vital feature of biodegradable and/or edible films, refers to the film's water resistance, integrity and suitability for food packaging. Films in contact with water during processing and storage need low water solubility, whereas packages with dry food to be dissolved in water or in hot food require high water solubility (Thakur et al., 2017; Wang et al., 2019). Plasticizers alter the polymer network via forming H-bonds or other non-covalent bonding, weaken the intermolecular forces between polymer chains and increase films' water solubility. The surface wetting, diffusion, swelling and disruption of the films are impacted by the plasticizers' hydrophilicity (Mujtaba et al., 2019). As shown in Fig. 4.a, all DT values were almost the same, indicating independence of this parameter from the type or concentration of the plasticizer used ($p > 0.05$). Pullulan films showed short DT probably due to the hydrophilic, hygroscopic, water-soluble nature and the low interaction density of pullulan. Our results were in agreement with previous studies (Galgatte et al., 2013; Gounga et al., 2007; Vuddanda et al., 2017).

"Biodegradable" refers to a substance that serves as a carbon source for the microbial growth (Mukuze et al., 2019). Films' biodegradability can be determined by their WL during decay in soil from moisture and microbial activity. Biodegradability is influenced by weather conditions, soil microorganisms' type, and film characteristics such as MC and density of the plant bioactive substances (Mujtaba et al., 2019). All the pullulan films incubated in soil showed high mass loss on the 15th day of degradation, as illustrated in Fig. 4.b. The process of soil degradation typically occurs in two stages. The initial stage involves biopolymers' hydrolysis and partial degradation. Pullulan, as a hydrophilic biopolymer, absorbs water rapidly through its -OH groups, leading to disrupted molecular interactions between pullulan chains and increased swelling. During the second stage, microbial enzymes break down substances and create polymer fragments, which allow soil microorganisms to absorb them. High water activity in pullulan films promotes the growth of soil microorganisms, leading to the enzyme production and degradation of the films through the utilization of pullulan as the carbon source. Plasticizers also underwent hydrolysis and metabolism in soil, causing a decrease in films' mass in the order of glycerol > sorbitol > fructose ($p < 0.05$). The films' WL rose as the plasticizer

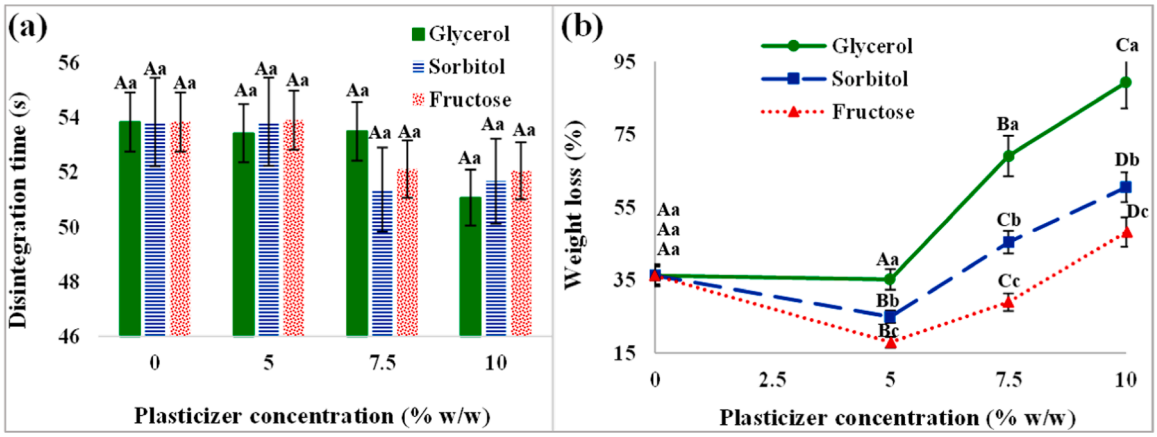

Fig. 4. Effect of plasticizer types and concentrations on films' disintegration time (a) and weight loss (b); Mean values with different uppercase letters in the same plasticizer type and lowercase letters at the same plasticizer concentration are significantly different ($p < 0.05$).

concentration increased ($p < 0.05$), with the exception of PG_5, PS_5 and PF_5. The inclusion of the plasticizers at > 5 % w/w in pullulan network increased the film's hygroscopic properties and enhanced the microbial growth, since plasticizers are hydrophilic, facilitate water absorption and increase films' water activity. Based on our results, pullulan films were environmentally friendly materials, which could decompose and disappear quickly in nature, unlike plastic. Comparable findings were documented previously (Li et al., 2020; Mujtaba et al., 2019; Mukuze et al., 2019).

3.6. Morphology

The films' surface and cross-sectional morphology showed the correlation between films' properties and their microstructures. SEM micrographs (Fig. 5) indicated similar morphological characteristics, with a continuous and packed microstructure, in PG_5, PS_5, PF_5 and control films. Furthermore, compared to the films containing sorbitol or fructose (at > 5 % w/w), with a smoother, more compact and more homogeneous appearance, the films plasticized with glycerol (at > 5 % w/w) had a more heterogeneous and porous texture with more small pinholes and apparent cracks probably due to the weak connection between glycerol and pullulan, creation of free space and the phase separation between the film components. In addition, by increasing plasticizer concentration from 5 % to 10 %w/w, films' homogeneity decreased probably due to the structural weakness. Consequently, SEM micrographs confirmed the limited plasticizing effect of glycerol among three plasticizers. Similar explanations have been published previously (Gounga et al., 2007; Vuddanda et al., 2017; Zhou et al., 2023).

3.7. Thermal behavior

The thermal properties of materials in food technology are crucial for understanding their thermal behavior and appropriateness for thermal processing (Meral et al., 2019). Glass transition temperature (Tg) is an important thermal characteristic of amorphous polymers, impacting polymeric films' structure, processing, and quality. Tg is the midpoint temperature of the observed alteration in heat capacity, where glassy materials transition to a rubbery state, causing significant changes in polymer mechanical properties (Vuddanda et al., 2017). As depicted in Fig. 6, control film, PG_5, PS_5 and PF_5 showed a Tg at 219, 223, 230 and 233 °C, respectively. The Tg of the films containing 7.5 and 10 % w/w glycerol were 191 and 170 °C, respectively. The Tg of 208 and 193 °C were observed for films plasticized with 7.5 and 10 % w/w sorbitol, respectively, while corresponding results for PF7.5 % and PF10 % were 214 and 201 °C, respectively. Therefore, all plasticizers at > 5 % w/w lowered the Tg of the pullulan films in the order of glycerol > sorbitol > fructose and in a concentration dependent manner by weakening non-covalent H-bonds between pullulan chains. This effect is intrinsically linked to the compatibility between plasticizers and polymers, as described by the free volume theory, as well as the Fox Eq. Free volume expansion, facilitated by plasticizer integration, enhances chain segment mobility and reduces Tg. Free volume refers to the unoccupied space between polymer chains, allowing segmental motion. When a plasticizer is added to a polymer matrix, it disrupts intermolecular interactions, increasing free volume. This enhanced free volume allows polymer chains to move more freely, reducing the rigidity of the material. As a result, the temperature at which the polymer transitions from a glassy state to a rubbery state (Tg) decreases. Plasticizers achieve this effect by reducing secondary forces, such as Van der Waals interactions or H-bonds, between polymer chains. With weaker interchain forces, molecular mobility increases, requiring less thermal energy to transition into the rubbery phase. Furthermore, the Fox Eq. can describe Tg variation based on the weight fraction of plasticizer and polymer compatibility. The Fox Eq. is an empirical relationship that describes the Tg of a polymer blend based on the weight fractions and Tg values of its components. From this Eq., as the plasticizer fraction increases, the Tg of the polymer-plasticizer blend decreases. This mathematical framework supports experimental observations that higher plasticizer content results in a lower Tg due to increased chain mobility and free volume. These findings were in line with our earlier outcomes, as well as reported results on plasticized films (Vuddanda et al., 2017).

4. Conclusions

The study showed that unplasticized pullulan films lack the necessary attributes to fulfill the requisite parameters for food packaging. In order to fabricate optimized food packaging films, pullulan was plasticized with diverse plasticizers (glycerol, sorbitol and fructose) at varying concentrations (5, 7.5 and 10 % w/w) and FFA, thickness, MC, TS, EAB, FE, WVP, OiR, O_2P, Tr_{280}, Tr_{660}, DT and WL were determined to elucidate the role of plasticizer type and concentration on pullulan films. It was revealed that plasticizers can change pullulan network and its end-use performance for food film packaging. Depending on which film properties are considered to be important, the type and concentration of plasticizer were optimized. Sorbitol at 7.5 % w/w was confirmed to have the best plasticization effect on the properties of pullulan, although the films containing glycerol or fructose were still of acceptable characteristics. This study had limitations in investigating the mixed plasticizers, antimicrobial properties, long-term stability under environmental fluctuations (effects of humidity and temperature variations on films' performance) and "*in situ*" functional bioactivity of the films, which will be the focus of our future research.

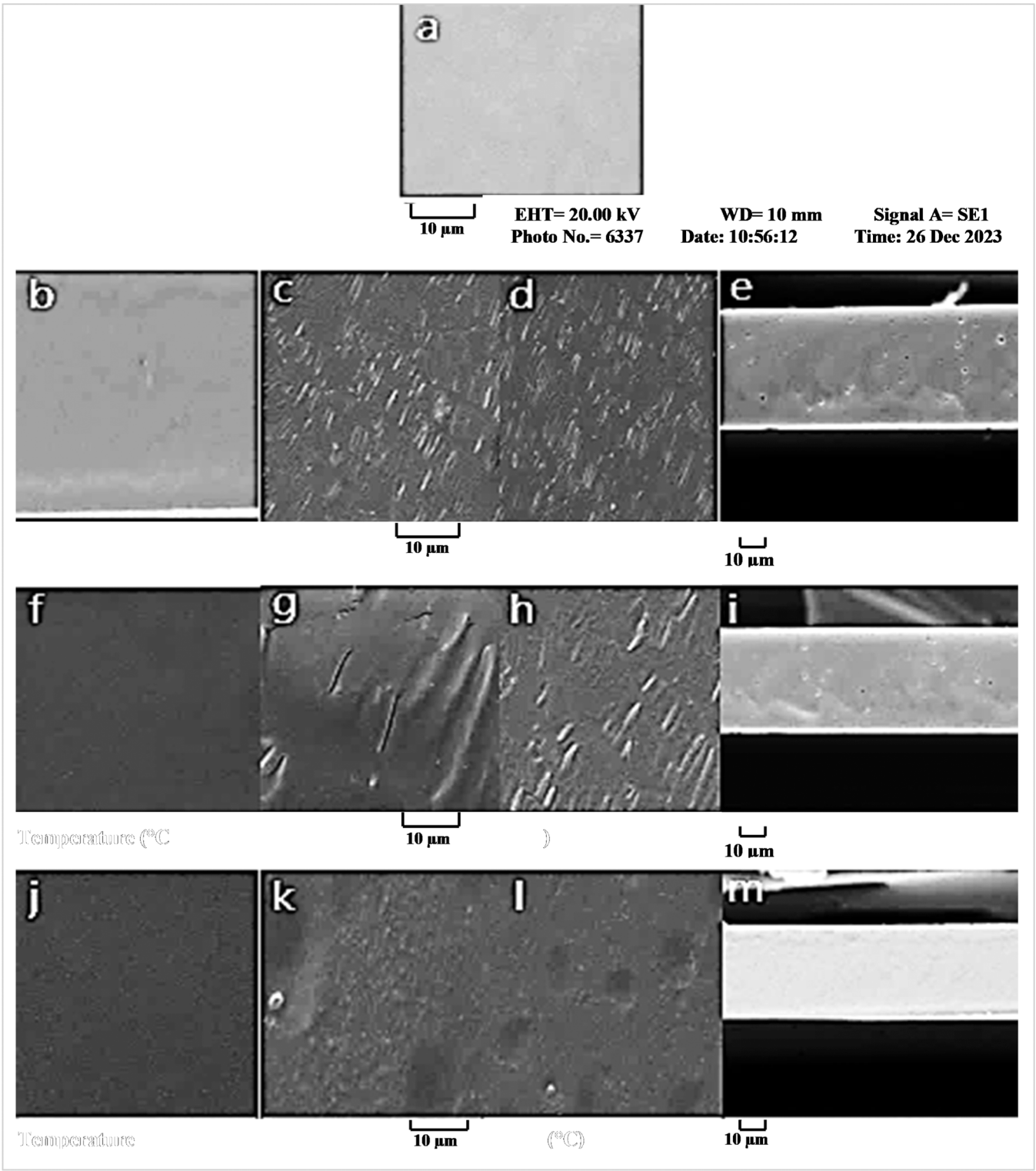

Fig. 5. SEM micrographs of the pullulan films; a is the surface view of the control film; b, c and d are the surface views of pullulan films containing 5, 7.5 and 10 % w/w glycerol, respectively; f, g and h are the surface views of pullulan films containing 5, 7.5 and 10 % w/w sorbitol, respectively; j, k and l are the surface views of pullulan films containing 5, 7.5 and 10 % w/w fructose, respectively; c, i and m are the cross section views of pullulan films containing 7.5 % w/w glycerol, sorbitol and fructose, respectively.

CRediT authorship contribution statement

Mohammad Reza Edalatian Dovom: Writing – review & editing, Supervision, Resources, Project administration, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Fakhri Shahidi:** Writing – review & editing, Supervision, Investigation, Funding acquisition, Conceptualization. **Ghazal Zamanidehyaghoubi:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Sahar Roshanak:** Writing – review & editing, Validation, Software, Resources, Methodology, Data curation. **Mohebbat Mohebbi:**

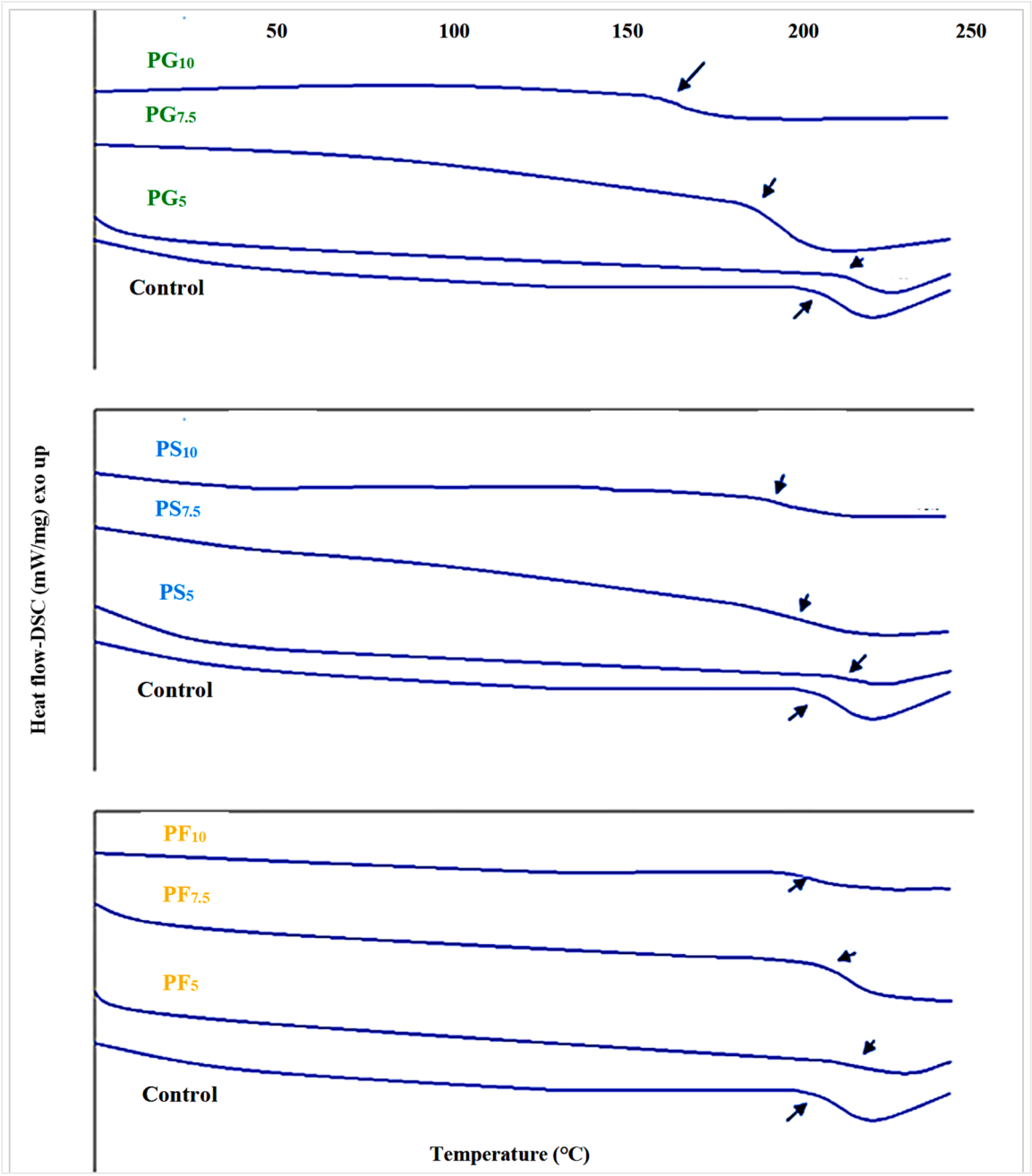

Fig. 6. DSC thermograms of pullulan films; PG_5, $PG_{7.5}$ and PG_{10} are pullulan films containing 5, 7.5 and 10 % w/w glycerol, respectively; PS_5, $PS_{7.5}$ and PS_{10} are pullulan films containing 5, 7.5 and 10 % w/w sorbitol, respectively; PF_5, $PF_{7.5}$ and PF_{10} are pullulan films containing 5, 7.5 and 10 % w/w fructose, respectively; Control is unplasticized pullulan film; Arrow mark (→) indicates Tg in the respective thermograms.

Writing – review & editing, Validation, Software, Resources, Methodology, Formal analysis, Data curation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This study was financially supported by Ferdowsi University of Mashhad, Iran [grant No. 3/54824].

Data Availability

Data will be made available on request.

References

Agrawal, M., Saraf, S., Pradhan, M., Patel, R. J., Singhvi, G., & Alexander, A. (2021). Design and optimization of curcumin loaded nano lipid carrier system using Box-Behnken design. *Biomedicine Pharmacotherapy, 141*, Article 111919. https://doi.org/10.1016/j.biopha.2021.111919

Akman, P. K., Bozkurt, F., Dogan, K., Tornuk, F., & Tamturk, F. (2021). Fabrication and characterization of probiotic *lactobacillus plantarum* loaded sodium alginate edible films. *Journal of Food Measurement and Characterization, 15*, 84–92. https://doi.org/10.1007/s11694-020-00619-6

Biao, Y., Yuxuan, C., Qi, T., Ziqi, Y., Yourong, Z., McClements, D. J., & Chongjiang, C. (2019). Enhanced performance and functionality of active edible films by

incorporating tea polyphenols into thin calcium alginate hydrogels. *Food Hydrocolloids, 97*, Article 105197. https://doi.org/10.1016/j.foodhyd.2019.105197
Chen, G., Zhang, B., Zhao, J., & Chen, H. (2014). Development and characterization of food packaging film from cellulose sulfate. *Food Hydrocolloids, 35*, 476–483. https://doi.org/10.1016/j.foodhyd.2013.07.003
El Miri, N., Aziz, F., Aboulkas, A., El Bouchti, M., Ben Youcef, H., & El Achaby, M. (2018). Effect of plasticizers on physicochemical properties of cellulose nanocrystals filled alginate bionanocomposite films. *Advances in Polymer Technology, 37*(8), 3171–3185. https://doi.org/10.1002/adv.22087
Farhan, A., & Hani, N. M. (2017). Characterization of edible packaging films based on semi-refined kappa-carrageenan plasticized with glycerol and sorbitol. *Food Hydrocolloids, 64*, 48–58. https://doi.org/10.1016/j.foodhyd.2016.10.034
Galgatte, U. C., Khanchandani, S. S., Jadhav, Y. G., & Chaudhari, P. D. (2013). Investigation of different polymers, plasticizers and superdisintegrating agents alone and in combination for use in the formulation of fast dissolving oral films. *International Journal of PharmTech Research, 5*(4), 1465–1472.
Gheribi, R., Taleb, Y., Perrin, L., Segovia, C., Brosse, N., & Desobry, S. (2023). Development of chitosan Green composites reinforced with hemp fibers: study of mechanical and barrier properties for packaging application. *Molecules, 28*(11), 4488. https://doi.org/10.3390/molecules28114488
González-Torres, B., Robles-García, M.Á., Gutiérrez-Lomelí, M., Padilla-Frausto, J. J., Navarro-Villarruel, C. L., Del-Toro-Sánchez, C. L., Rodríguez-Félix, F., Barrera-Rodríguez, A., Reyna-Villela, M. Z., & Avila-Novoa, M. G. (2021). Combination of sorbitol and glycerol, as plasticizers, and oxidized starch improves the physicochemical characteristics of films for food preservation. *Polymers, 13*(19), 3356. https://doi.org/10.3390/polym13193356
Gounga, M. E., Xu, S.-Y., & Wang, Z. (2007). Whey protein isolate-based edible films as affected by protein concentration, glycerol ratio and pullulan addition in film formation. *Journal of Food Engineering, 83*(4), 521–530. https://doi.org/10.1016/j.jfoodeng.2007.04.008
Hassan, A. H., & Cutter, C. N. (2020). Development and evaluation of pullulan-based composite antimicrobial films (CAF) incorporated with nisin, thymol and lauric arginate to reduce foodborne pathogens associated with muscle foods. *International Journal of Food Microbiology, 320*, Article 108519. https://doi.org/10.1016/j.ijfoodmicro.2020.108519
Islam, H. B. M. Z., Susan, M. A. B. H., & Imran, A. B. (2020). Effects of plasticizers and clays on the physical, chemical, mechanical, thermal, and morphological properties of potato starch-based nanocomposite films. *ACS Omega, 5*(28), 17543–17552. https://doi.org/10.1021/acsomega.0c02012
Kanmani, P., & Rhim, J.-W. (2014). Properties and characterization of bionanocomposite films prepared with various biopolymers and ZnO nanoparticles. *Carbohydrate Polymers, 106*, 190–199. https://doi.org/10.1016/j.carbpol.2014.02.007
Kurt, A., & Kahyaoglu, T. (2014). Characterization of a new biodegradable edible film made from salep glucomannan. *Carbohydrate Polymers, 104*, 50–58. https://doi.org/10.1016/j.carbpol.2014.01.003
Lakhawat, S. S., Sharma, P. K., Kumar, S., Pandey, A., & Kumar, V. (2023). Deciphering the plasticizers for the development of polysaccharide based biodegradable edible coatings. *Current Nutrition Food Science, 19*(6), 582–589. https://doi.org/10.2174/1573401318666220908105130
Li, S., Ma, Y., Ji, T., Sameen, D. E., Ahmed, S., Qin, W., Dai, J., Li, S., & Liu, Y. (2020). Cassava starch/carboxymethylcellulose edible films embedded with lactic acid bacteria to extend the shelf life of banana. *Carbohydrate Polymers, 248*, Article 116805. https://doi.org/10.1016/j.carbpol.2020.116805
Liu, Y., Liu, Y., Han, K., Cai, Y., Ma, M., Tong, Q., & Sheng, L. (2019). Effect of nano-TiO_2 on the physical, mechanical and optical properties of pullulan film. *Carbohydrate Polymers, 218*, 95–102. https://doi.org/10.1016/j.carbpol.2019.04.073
Lu, X., Chen, Z., Ma, Q., Mu, J., Li, X., & Liu, H. (2022). Preparation and characterization of yellow peach peel/sodium alginate/glycerol antioxidant film applicable for oil package. *Polymers, 14*(9), 1693. https://doi.org/10.3390/polym14091693
Memiş, S., Tornuk, F., Bozkurt, F., & Durak, M. Z. (2017). Production and characterization of a new biodegradable fenugreek seed gum based active nanocomposite film reinforced with nanoclays. *International Journal of Biological Macromolecules, 103*, 669–675. https://doi.org/10.1016/j.ijbiomac.2017.05.090
Meral, R., Alav, A., Karakas, C., Dertli, E., Yilmaz, M. T., & Ceylan, Z. (2019). Effect of electrospun nisin and curcumin loaded nanomats on the microbial quality, hardness and sensory characteristics of rainbow trout fillet. *LWT, 113*, Article 108292. https://doi.org/10.1016/j.lwt.2019.108292
Mihaly-Cozmuta, A., Peter, A., Craciun, G., Falup, A., Mihaly-Cozmuta, L., Nicula, C., Vulpoi, A., & Baia, M. (2017). Preparation and characterization of active cellulose-based papers modified with TiO_2, ag and zeolite nanocomposites for bread packaging application. *Cellulose, 24*, 3911–3928. https://doi.org/10.1007/s10570-017-1383-x
Monjazeb Marvdashti, L., Koocheki, A., & Yavarmanesh, M. (2019). Characterization, release profile and antimicrobial properties of bioactive polyvinyl alcohol-*alyssum homolocarpum* seed gum-nisin composite film. *Food Biophysics, 14*, 120–131. https://doi.org/10.1007/s11483-018-09562-y
Moradi, Z., Esmaiili, M., & Almasi, H. (2019). Development and characterization of kefiran-Al_2O_3 nanocomposite films: morphological, physical and mechanical properties. *International Journal of Biological Macromolecules, 122*, 603–609. https://doi.org/10.1016/j.ijbiomac.2018.10.193
Mujtaba, M., Koc, B., Salaberria, A. M., Ilk, S., Cansaran-Duman, D., Akyuz, L., Cakmak, Y. S., Kaya, M., Khawar, K. M., & Labidi, J. (2019). Production of novel chia-mucilage nanocomposite films with starch nanocrystals; an inclusive biological and physicochemical perspective. *International Journal of Biological Macromolecules, 133*, 663–673. https://doi.org/10.1016/j.ijbiomac.2019.04.146
Mukuze, S., Magut, H., & Mkandawire, F. L. (2019). Comparison of fructose and glycerol as plasticizers in cassava bioplastic production. *Advanced Journal of Graduate Research, 6*(1), 41–52. https://doi.org/10.21467/ajgr.6.1.41-52
Pezik, E., Gulsun, T., Sahin, S., & Vural, I. (2021). Development and characterization of pullulan-based orally disintegrating films containing amlodipine besylate. *European Journal of Pharmaceutical Sciences, 156*, Article 105597. https://doi.org/10.1016/j.ejps.2020.105597
Rostami, H., & Esfahani, A. A. (2019). Development a smart edible nanocomposite based on mucilage of melissa officinalis seed/montmorillonite (MMT)/curcumin. *International Journal of Biological Macromolecules, 141*, 171–177. https://doi.org/10.1016/j.ijbiomac.2019.08.261
Roy, S., & Rhim, J.-W. (2020). Carboxymethyl cellulose-based antioxidant and antimicrobial active packaging film incorporated with curcumin and zinc oxide. *International Journal of Biological Macromolecules, 148*, 666–676. https://doi.org/10.1016/j.ijbiomac.2020.01.204
Saberi, B., Vuong, Q. V., Chockchaisawasdee, S., Golding, J. B., Scarlett, C. J., & Stathopoulos, C. E. (2016). Mechanical and physical properties of pea starch edible films in the presence of glycerol. *Journal of Food Processing and Preservation, 40*(6), 1339–1351. https://doi.org/10.1111/jfpp.12719
Shah, A., Ashames, A. A., Buabeid, M. A., & Murtaza, G. (2020). Synthesis, in vitro characterization and antibacterial efficacy of moxifloxacin-loaded chitosan-pullulan-silver-nanocomposite films. *Journal of Drug Delivery Science and Technology, 55*, Article 101366. https://doi.org/10.1016/j.jddst.2019.101366
Silva, N. H., Vilela, C., Almeida, A., Marrucho, I. M., & Freire, C. S. (2018). Pullulan-based nanocomposite films for functional food packaging: exploiting lysozyme nanofibers as antibacterial and antioxidant reinforcing additives. *Food Hydrocolloids, 77*, 921–930. https://doi.org/10.1016/j.foodhyd.2017.11.039
Tabasum, S., Noreen, A., Maqsood, M. F., Umar, H., Akram, N., Chatha, S. A. S., & Zia, K. M. (2018). A review on versatile applications of blends and composites of pullulan with natural and synthetic polymers. *International Journal of Biological Macromolecules, 120*, 603–632. https://doi.org/10.1016/j.ijbiomac.2018.07.154
Thakur, R., Saberi, B., Pristijono, P., Stathopoulos, C. E., Golding, J. B., Scarlett, C. J., Bowyer, M., & Vuong, Q. V. (2017). Use of response surface methodology (RSM) to optimize pea starch–chitosan novel edible film formulation. *Journal of Food Science and Technology, 54*, 2270–2278. https://doi.org/10.1007/s13197-017-2664-y
Tian, H., Liu, D., Yao, Y., Ma, S., Zhang, X., & Xiang, A. (2017). Effect of sorbitol plasticizer on the structure and properties of melt processed polyvinyl alcohol films. *Journal of Food Science, 82*(12), 2926–2932. https://doi.org/10.1111/1750-3841.13950
Tong, Q., Xiao, Q., & Lim, L.-T. (2013). Effects of glycerol, sorbitol, xylitol and fructose plasticisers on mechanical and moisture barrier properties of pullulan–alginate–carboxymethylcellulose blend films. *International Journal of Food Science and Technology, 48*(4), 870–878. https://doi.org/10.1111/ijfs.12039
Vuddanda, P. R., Montenegro-Nicolini, M., Morales, J. O., & Velaga, S. (2017). Effect of plasticizers on the physico-mechanical properties of pullulan based pharmaceutical oral films. *European Journal of Pharmaceutical Sciences, 96*, 290–298. https://doi.org/10.1016/j.ejps.2016.09.011
Wang, L., Xue, J., & Zhang, Y. (2019). Preparation and characterization of curcumin loaded caseinate/zein nanocomposite film using pH-driven method. *Industrial Crops and Products, 130*, 71–80. https://doi.org/10.1016/j.indcrop.2018.12.072
Wu, H., Lei, Y., Zhu, R., Zhao, M., Lu, J., Xiao, D., Jiao, C., Zhang, Z., Shen, G., & Li, S. (2019). Preparation and characterization of bioactive edible packaging films based on pomelo peel flours incorporating tea polyphenol. *Food Hydrocolloids, 90*, 41–49. https://doi.org/10.1016/j.foodhyd.2018.12.016
Wu, W., Liu, L., Zhou, Y., & Shao, P. (2024). Highly ammonia-responsive starch/PVA film with gas absorption system as the 'bridge' for visually spoilage monitoring of animal-derived food. *Food Chemistry, 430*, Article 137032. https://doi.org/10.1016/j.foodchem.2023.137032
Wu, W., Zhou, Y., Pan, J., Wu, Y., Goksen, G., & Shao, P. (2023). Multibranched flower-like ZnO anchored on pectin/cellulose nanofiber aerogel skeleton for enhanced comprehensive antibacterial capabilities. *Carbohydrate Polymers, 322*, Article 121320. https://doi.org/10.1016/j.carbpol.2023.121320
Wu, C., Zhu, Y., Wu, T., Wang, L., Yuan, Y., Chen, J., Hu, Y., & Pang, J. (2019). Enhanced functional properties of biopolymer film incorporated with curcurmin-loaded mesoporous silica nanoparticles for food packaging. *Food Chemistry, 288*, 139–145. https://doi.org/10.1016/j.foodchem.2019.03.010
Xin, S., Xiao, L., Dong, X., Li, X., Wang, Y., Hu, X., Sameen, D. E., Qin, W., & Zhu, B. (2020). Preparation of chitosan/curcumin nanoparticles based zein and potato starch composite films for *schizothorax prenati* fillet preservation. *International Journal of Biological Macromolecules, 164*, 211–221. https://doi.org/10.1016/j.ijbiomac.2020.07.082
Yang, Y., Liu, H., Wu, M., Ma, J., & Lu, P. (2020). Bio-based antimicrobial packaging from sugarcane bagasse nanocellulose/nisin hybrid films. *International Journal of Biological Macromolecules, 161*, 627–635. https://doi.org/10.1016/j.ijbiomac.2020.06.081
Zhou, K., Yang, Y., Zheng, B., Yu, Q., Huang, Y., Zhang, N., Rama, S. M., Zhang, X., Ye, J., & Xiao, M. (2023). Enhancing pullulan soft capsules with a mixture of glycerol and sorbitol plasticizers: A multi-dimensional study. *Polymers, 15*(10), 2247. https://doi.org/10.3390/polym15102247