



Plasticized films based on PLA and PHB: from the choice of plasticizer to the packaging prospects

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Abstract

PLA- and PHB-based films were plasticized with triacetin (TA), triethyl citrate (TEC), tributyl-o-acetyl citrate (TBAC) in concentrations ranging from 1 to 10 wt.%. We found that introduction of TA and TEC affected the surface of PLA films, leading to the formation of closed pores and cavities, whereas TBAC did not noticeably affect the surface. Upon plasticization, the elongation at break of PLA films increased up to 30-fold. The introduction of plasticizers caused less than a two-fold change in the values for PHB films. The plasticized PLA and PHB films were characterized by lower melting points (around 143–144 °C and 166–167 °C, respectively) compared to the non-plasticized films (147 °C and 168 °C). Following incubation in aqueous model solutions (5% sodium chloride, 2% citric acid, 0.3% lactic acid), the plasticizers gradually migrated from the films into the environment, reaching 0.0034 mg·mg⁻¹. This migration led to a reduction in the films' mechanical properties: at pH 6.0, the tensile strength and elongation at break decreased by a factor of 1.3–1.5, while at pH 2.6, a fivefold decrease was observed. The shelf life of chicken fillets was extended up to one week without any obvious change in sensory characteristics. The plasticizer was detected in chicken fillets at a very low concentration (approximately 2.1 µg/g) on day 3 but was no longer detectable by day 7 of the experiment.

Key findings

- PLA- and PHB-based films were plasticized with triacetin (TA), triethyl citrate (TEC), and tributyl-o-acetyl citrate (TBAC).
- Chicken fillets were successfully preserved in TBAC plasticized films for up to one week.
- The plasticizer was detected in chicken fillets at a concentration of up to 2.1 µg/g.

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1. Introduction

The annual volume of food waste in Russia is estimated at 17.9 million tons, while the food and process industries generate 30 million tons of secondary raw materials and waste. Most food waste (approximately 71%) is generated by households, with retail and public catering accounting for the remaining 29% [1]. Food spoilage is primarily

caused by microbial growth, which leads to the oxidation of organic matter and the accumulation of toxic metabolic by-products. Food packaging techniques such as heat treatment, high-pressure processing, vacuum packaging, and the use of petroleum-based synthetic materials, primarily petroleum-based polymers like polyethylene (PE) and polypropylene (PP) with antibacterial or fungicidal additives, show great promise in reducing the risks of foodborne dis-

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eases. However, the non-biodegradable nature of these materials leads to significant environmental pollution, posing a serious global challenge. Consequently, developing sustainable alternatives has become imperative.

One promising solution is the development of biodegradable, eco-friendly packaging. Among biodegradable polymers, polymers of hydroxycarboxylic acids (polylactide (PLA), polyhydroxyalkanoates (PHAs), poly- ϵ -caprolactone), polymers of phthalic and adipic acids, starch compounds, polybutylene succinate, etc., are of particular interest, accounting for more than 55% of the world's bioplastics production [2]. The key advantage of biopolymers over PE and PP lies in their renewable origin and inherent biodegradability. This combination significantly reduces the carbon footprint and environmental burden.

PLA is a polymer obtained by polymerization of lactic acid with a subsequent ring-opening reaction resulting in formation of polylactic acid. In addition to being recyclable and compostable, PLA has a high molecular weight (up to 200 kDa) and exhibits high transparency [3]. The properties of PLA can change from crystalline to amorphous depending on the ratio of monomers. PLA is not only biocompatible and biodegradable, but also exhibits mechanical and barrier properties comparable to those of conventional synthetic polymers [4]. PLA has an oxygen permeability approximately 5 to 10 times lower than that of LDPE and PP [5]. This can be attributed to a denser packing of polymer chains and the presence of polar groups. In their study, Bala et al. demonstrated that polylactic acid bags reinforced with nanoclays are a viable alternative to fossil-based polymers (PE and PP) for reducing climate change impact and fossil resource consumption [6].

Polyhydroxyalkanoates (PHAs) are natural polyesters obtained via bacterial fermentation of carbohydrates (glucose, molasses, or glycerol) under nitrogen-limiting conditions [7]. The most common representative of PHA is poly-3-hydroxybutyrate (PHB), which is a polyester of 3-hydroxybutyric acid. PHB exhibits good UV resistance and favorable optical properties. Its melting and glass-transition temperatures are approximately 180 °C and 55 °C, respectively. Its barrier properties against moisture and gases surpass those of polypropylene, making it a promising material for packaging applications. [5]. Despite exhibiting a crystallinity of over 50%, PHB is thermally unstable, and its molecular weight can decrease significantly between the glass transition and melting temperatures, substantially limiting its processability. [8]. Copolymerization with other PHAs and the addition of plasticizers, nucleating agents, and stabilizers are common strategies to overcome this disadvantage [9].

Despite their advantages, the application of biodegradable polymers in packaging faces significant challenges. These include inadequate moisture and gas barrier properties compared to high-barrier synthetic materials (e.g., EVOH), limited thermal stability, lower mechanical strength, and higher production costs relative to conven-

tional polymers [10]. Nevertheless, ongoing research and material modifications are successfully bridging this performance gap for many packaging applications where environmental safety is a decisive priority.

A common strategy to enhance the flexibility, elasticity, and processability of these materials is the introduction of plasticizers, which increase the mobility of polymer chains. However, due to their low molecular weight, plasticizers can migrate to the surface of the polymer matrix, potentially contaminating any materials that come into contact with the plasticized polymer. Consequently, choosing an appropriate plasticizer that exhibits low volatility and moderate molecular weight is crucial for applications in food packaging. Commonly used biodegradable plasticizers for PLA and PHAs include oligomeric lactic acid, glycerol, polyethylene glycol, tributyl citrate, acetyl tributyl citrate, triethyl citrate, acetyl triethyl citrate, and triacetin. All of these substances are recognized as effective [11–14].

Research indicates that these plasticizers can significantly enhance the elongation at break of PLA and PHB by facilitating chain mobility and diminishing the interaction forces caused by hydrogen bonding within the polymer matrix [15–17]. However, increasing plasticizer concentration also raises the water permeability of PLA films. This effect is due to the strong affinity of water molecules for PLA [18–20]. Optimal incorporation of plasticizers can enhance the flexibility of PLA without causing a substantial increase in water permeability.

The specific effects of plasticizers on these polymers have been described in a number of recent studies devoted to changing the properties of PLA, PHAs, and their various blends. It is noteworthy that while plasticizer addition typically reduces material strength (decreasing Young's modulus and tensile strength), it also enables the mechanical properties of flexible biopolymer films to approach those of low-density polyethylene (LDPE), all while retaining the key advantage of biodegradability.

The aim of this work was to develop a series of plasticized PLA- and PHB-based biodegradable films, characterize their packaging-relevant properties, and, based on this data, select the most promising composition for testing as packaging for chicken fillet storage. This study employed three biodegradable, non-toxic plasticizers: triacetin, triethyl citrate, and tributyl *o*-acetyl citrate. This study presents a comprehensive analysis of plasticized films, establishing clear correlations between their mechanical/structural properties and their performance as food packaging materials—an aspect often overlooked in prior research.

2. Materials and Methods

2.1. Polymers, plasticizers and other reagents

Two commercial biodegradable polymers were used: (1) polylactide (PLA) (NatureWorks, USA) with a weight-average molecular weight (M_w) of 119 kDa, 60% crystal-

linity (C_x), and a melting point (T_m) of 170 °C; and (2) poly-3-hydroxybutyrate (PHB) (Biomer, Schwabach, Germany) characterized by an M_w of 616 kDa and a $C_x = 60\%$. The plasticizers used were:

Triacetin (TA) (Sigma-Aldrich, USA): density (ρ) 1.16 g/ml, boiling point (T_b) 258 °C, molecular weight (M) 218.21 g/mol;

Triethyl citrate (TEC) (Acros Organics, Germany): $\rho = 1.14$ g/ml, $T_b = 294$ °C, $M = 276.28$ g/mol;

Tributyl O-acetylcitrate (ATBC) (Sigma-Aldrich, USA): $\rho = 1.05$ g/ml, $T_b = 327$ °C, $M = 402.48$ g/mol.

The films were prepared using trichloromethane (chloroform) as the solvent ($\rho = 1.49$ g/ml, $M = 119.38$ g/mol, OOO Ekroskhim, Russia).

2.2. Preparation of polymer films

Polymer films were prepared by solution casting (Figure 1). Briefly, PLA or PHB (2 wt.%) was dissolved in chloroform with heating at 50 °C until complete dissolution. The resulting solution was poured onto a degreased Petri dish and allowed to dry for 48 h to ensure full solvent evaporation. Plasticized films were obtained using an identical procedure, but one of the plasticizers (TA, TEC, TBAC) was added to the solution in the amount corresponding to one of the concentrations (1, 3, 5 and 10 wt.% of polymer content), and the solution was thoroughly mixed on the magnetic stirrer. The thickness of the films was measured with a micrometer.

2.3. Study of polymer film samples

2.3.1. Surface structure analysis of polymer films

Scanning electron microscopy (SEM) was performed on a Hitachi S5500 microscope (Japan) to characterize the microstructure of the films. The samples were sputter-coated with platinum (10 mA, 40 s) using an Emitech K575X unit. The pore sizes of the prepared polymer films were measured based on the obtained SEM images using ImageJ software (v.1.54k) for Windows.

2.3.2. Differential mechanical, thermogravimetric and FT-IR analyses

A thermomechanical study of the viscoelastic properties of the sample films was conducted using a dynamic mechanical analyzer Q800 (TA Instruments, USA). The measurements of the storage modulus (E') of a sample was carried out using a tensile clamp without heating. The frequency of dynamic loading of the sample was 1 Hz, and the relative deformation was less than 0.1%.

Thermal analysis was performed using an SDT Q600 thermal analyzer (TA Instruments, USA). The thermograms were obtained by heating samples in platinum crucibles at a rate of 20 K/min to temperatures between 600 and 800 °C under a 50 ml/min air flow.

FTIR-spectra were captured by continuous scanning during the thermogram recording in the wavelength range between 4000 and 500 cm^{-1} . A series of scans was processed using the Omnic 7 software, and the absorbance of the released gases was plotted as a function of time.

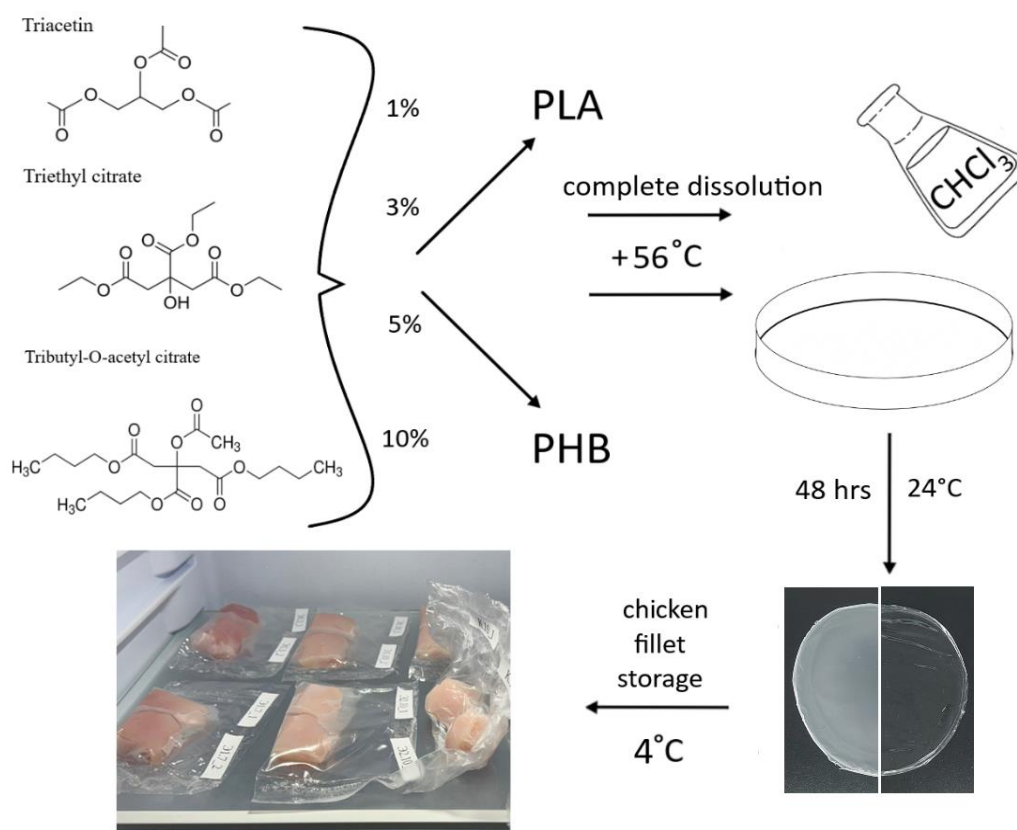


Figure 1 Schematic visualization of the preparation of the studied films.

2.3.3. Effect of incubation in different model solutions on the mechanical properties of films

The obtained plasticized films, demonstrating the best mechanical characteristics according to GOST R 57432-2017 requirements [21], were cut into strips with 2.0x0.5 cm in size. The strips were incubated in 40 ml of one of the model solutions (sodium chloride 5%, citric acid 2%, lactic acid 0.3%), simulating the storage of various food products (salted or smoked meat or fish, fruit, berry or vegetable products and fresh meat or fish, respectively) [22] at room temperature without direct sunlight. Distilled water was used as a control solution, which also simulates the storage of food products according to the aforementioned regulations. After predetermined time periods (1, 3 and 10 days), the films were removed from the solutions, dried at room temperature for 24 h and analyzed by DMA (described above).

2.3.4. Migration of plasticizers into the model solutions

We quantified plasticizer migration for PLA films containing 1% of TBAC after 10 days of incubation in model solutions (the method is described above). After incubation, the residual amount of plasticizer in the film samples was determined by gas chromatography-mass spectrometry (GC-MS). The films were preliminarily dissolved in 1 ml of chloroform, precipitated with 9 ml of hexane, centrifuged for 5 min at 3000 rpm, and the supernate was used for the analysis.

The GC-MS analysis was carried out using Agilent 6890N gas chromatograph with Agilent 5975C mass spectrometer (USA). Agilent VF-200ms polytrifluoropropylmethylsiloxane column was installed (length 60 m, internal diameter 250 μm , sorbing layer thickness 0.10 μm). Helium served as the carrier gas at a constant flow rate of 1.2 $\text{ml}\cdot\text{min}^{-1}$. Injection was performed in a splitless mode. The inlet and transfer line temperatures were set to 220 $^{\circ}\text{C}$ and 230 $^{\circ}\text{C}$, respectively. The temperature was programmed as follows: 55 $^{\circ}\text{C}$ (hold 3 min), ramp to 310 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$, hold 5 min. The total run time was 33.5 min. Electron impact (70 eV) was used for sample ionization. The characteristic ion for tributyl acetyl citrate with m/z 259 was analyzed. The release time of TBAC was approximately 25.5 min, therefore the solvent delay was set at 24 min. The results were processed using MSD ChemStation software (version E.02.02.1431). Concentrations were determined using a calibration curve generated from external TBAC standards at concentrations of 1, 10, and 100 $\mu\text{g}/\text{mL}$.

2.3.5. Film porosity and water vapor permeability

The porous structure of the samples was studied using a Porolux 1000 capillary flow porometer (POROMETER, Belgium). The operating principle of the porometer is based on the wetting fluid shift using a gas flow with a

stepwise increase in pressure and its stabilization. Porosity analysis involves measuring two curves: a wet curve from the sample after soaking with a wetting fluid (PorefilTM, surface tension = 15.9 dynes/cm), and a dry curve from the same sample after drying. The intersection point (pressure value) of the wet curve and the dry curve (taken with a coefficient of 0.5) corresponds to the average pore diameter in the sample.

Film permeability was measured using a setup in which distilled water was pumped through the film under pressure, which was provided by a compressor, regulated by AW20-F01C-A B pressure regulator (SMC, Japan) and monitored by ISE40A precision pressure sensor (SMC, Japan). The volume of water passing through the film was determined using GX-800 laboratory balance (AND, Japan) by an automatic mass record after a specified period of time. The volumetric flow (velocity) J of water (in $\text{m}^3\cdot\text{m}^{-2}\cdot\text{min}^{-1}$) was determined as the volume of water passing through the film in one minute (in m^3/min) divided by the film area (in m^2). Permeability K was calculated using the following equation:

$$K = J/\Delta P, \quad (1)$$

where ΔP is the pressure above the film (in bar). For each ΔP the measurements were made until a constant flow value was achieved.

2.4. Chicken fillet storage in plasticized biodegradable films

Fresh chilled chicken fillet (JSC Solgon, Russia), purchased in a local retail store, was chosen as the test product for the storage test. PLA film, and PLA/TBAC 1% film were used as test materials. The average thickness of the films was $23.0 \pm 1.0 \mu\text{m}$. Conventional polyethylene (PE) film was used as a control. Before testing, the films were sterilized under UV light for 15 minutes. A control wash was collected from the film surfaces to determine the initial microbial contamination.

Chicken fillets were sliced into portions weighing 13–16 g each. Two portions were placed into each package, which was made from a 15 cm \times 15 cm film. The films with the slices were thermally sealed to ensure hermeticity. All samples were then stored in a pre-washed refrigerator at 4–5 $^{\circ}\text{C}$ for 7 days. Samples were taken for analysis on days 3 and 7 to determine microbial contamination and evaluate sensory characteristics.

For each sample, the chicken portion was aseptically removed from the packaging film. It was then homogenized for 60 sec using a blender sterilized with 70% ethanol; all handling was performed in a microbiological box. The homogenate was transferred to 90 mL of sterile saline buffer and shaken at 150 rpm for 15 min until the complete homogeneity of the suspension. Serial dilutions of the suspension were plated (0.1 mL of the 10^3 and 10^4 dilutions) onto PCA, Endo, and MRS agar. Petri dishes

were incubated at 37 °C (48 h) for PCA and Endo, or at 32 °C (72 h) for MRS. The CFU/g for each microbial group (total aerobes, coliforms/enterobacteria, and lactic acid bacteria) was determined from colony counts.

To determine the residual plasticizer concentration in the fillet slices, a sample was weighed, chopped with a knife, placed in a 200 ml flask, and chloroform was added at a volume of 5 ml per 1 g of a fillet sample. The mixture was stirred for 15 min, and then sonicated at 25 °C for 15 min. After sonication, 15 ml of the mixture were centrifuged at 3000 rpm for 10 min. The concentration of plasticizer in the resulting supernatant was determined using gas chromatography as described above (Section 2.3.4.).

Sensory analysis was performed by three independent experts. They scored the chicken samples according to the following predetermined attributes: (1) appearance (presence of slime, sheen), (2) color (light pink to gray scale), (3) odor (fresh to sour), (4) texture (moisture, elasticity, stickiness), and (5) fat color (white/pale to yellow). Each attribute was rated on a five-point scale: 5 = excellent, 4 = good, 3 = satisfactory, 2 = poor, 1 = very poor.

2.5. Data processing

Statistical analysis was conducted using Microsoft Excel 2010. Results are expressed as mean values with their standard deviations. Significant differences between mean values were tested using Student's *t* test (significance level: $p = 0.05$).

3. Results and Discussion

3.1. Surface properties of plasticized films

Biodegradable polymer films with varying plasticizer content and a thickness of 18.7–27.3 μm were prepared. The surface structures of pure PLA and PHB films and the corresponding films with the addition of TA, TEC and TBAC in the amount of 5 wt.% were studied by SEM. The SEM analysis visualizes the impact of both polymer and plasticizer type—specifically, triacetin (TA), triethyl citrate (TEC), and tributyl citrate (TBAC)—on the resulting surface morphology. The neat PLA (Figure 2a) exhibits the smoothest and most uniform surface, with only sporadic submicron defects, indicative of a dense, coherent structure. In contrast, the neat PHB (Figure 2e) possesses a rough, textured morphology characterized by alternating regions of varying density and numerous micropores, which reflects its complex crystalline organization.

Addition of TA (Figure 2b) and TEC (Figure 2c) to PLA films resulted in the appearance of altered heterogeneous areas on the film surface. The corresponding zones displayed looseness and porosity with varying degrees of deepening. The appearance of cavities and pores ranging in size from 20 to 300 nm was also noted. We attribute these surface irregularities to non-uniform solvent evaporation, which caused local variations in the solvent:polymer:plasticizer ratio. This effect was likely in-

fluenced by the plasticizer's specific physical properties and its interaction with the polymer. When TBAC—which has the highest molecular weight among the plasticizers tested—was added to PLA, the resulting film surface became smooth and visually similar to that of neat PLA (Figure 2d). This morphological resemblance underscores the high compatibility between PLA and TBAC. In summary, TA and TEC substantially increase the porosity and surface heterogeneity of PLA films. In contrast, TBAC integrates most effectively into the PLA matrix, preserving its native smooth morphology to the greatest extent.

The addition of TA and TEC to PHB films caused fewer changes in the surface compared to PLA films, but resulted in a 1.5–2 fold increase in the number of pores (Figure 2f, 2g). In PHB/TA films the pore size slightly decreased compared to pure PHB films and ranged from 10 to 200 nm in size, whereas in PHB/TEC films the pore size ranged from 30 to 400 nm. The surface of PHB/TBAC films was similar to that of pure PHB film and the PHB/plasticizer films, but the pore size had reached 1 μm (Figure 2h). Similarly, the addition of TA and TEC (Figure 2f, 2g) accentuates surface roughness and introduces fine pores. In contrast, TBAC (Figure 2h) maintains the inherent roughness of neat PHB (Figure 2e) but renders the structure more open and porous.

Porosity analysis showed that the films were non-macroporous and lacked through-pores. The bubble point pressure—the pressure at which the first continuous air flow through the sample was detected—varied among the compositions, indicating different maximum pore sizes. The highest bubble point pressure was 24.7 atm for PLA/TBAC 5%, corresponding to the smallest maximum pore size of 20 nm. The lowest was 7.8 atm for PHB/TEC 5%, corresponding to a maximum pore size of 58 nm. No pores larger than these maximums were detected, as exceeding this pressure leads to irreversible sample degradation, preventing the measurement of smaller pores.

3.2. Mechanical properties of pure and plasticized PLA and PHB films

A major limitation to the wider application of PLA and PHB is their inherent brittleness, which restricts their utility in both consumer products and advanced material applications. Thus, the introduction of plasticizers is considered to be one of the strategies for improving the properties of PLA and PHB.

The results of DMA showed that the introduction of plasticizers clearly has a different effect on the tensile strength and elongation at break values of PLA and PHB. This result is attributed to the higher crystallinity and molecular weight of PHB (67%, 616 kDa) compared to PLA (55%, 180 kDa), combined with the specific chemical structures and properties of the plasticizers. The addition of TA to PLA films gradually decreased the tensile strength from 57 MPa (pure PLA) to 20 MPa (10% TA).

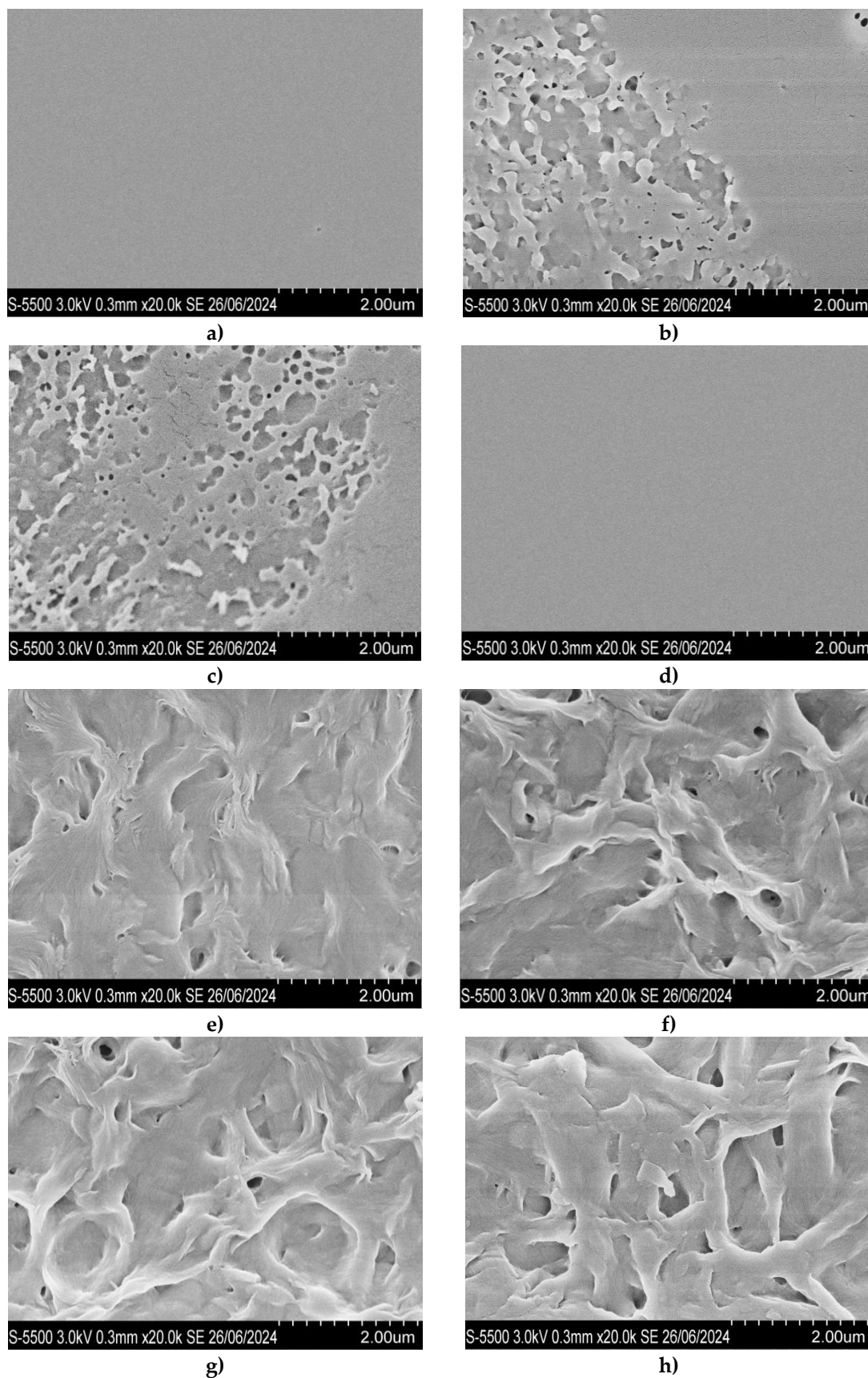


Figure 2 SEM images of polymeric and polymer /plasticizer films (x20k magnification): PLA (a), PLA/TA 5% (b), PLA/TEC 5% (c), PLA/TBAC 5% (d), PHB (e), PHB/TA 5% (f), PHB/TEC 5% (g), PHB/TBAC 5% (h).

Simultaneously, the elongation at break rose dramatically from 15% to 515% (Table 1), with the most substantial increase occurring between 3 and 5 wt.% TA. The ad-

dition of 10 wt.% TA to PLA films shows the highest elongation at break (Table 1).

Table 1 Change in mechanical properties of PLA and PHB films depending on the added amount of plasticizers (data from other similar studies is also provided).

Plasticizer concentration, wt.%	PLA		PHB	
	Tensile strength, MPa	Elongation at break, %	Tensile strength, MPa	Elongation at break, %
0 (control)	57.1 ± 10.5	15.4 ± 1.9	42.4 ± 8.5	4.3 ± 0.3
TA				
1	38.6 ± 3.8	20.5 ± 2.3	65.4 ± 20.9	8.1 ± 0.6
3	31.7 ± 2.3	21.7 ± 2.7	81.3 ± 23.4	6.6 ± 0.2
5	28.3 ± 4.0	398.4 ± 51.1	28.5 ± 3.8	3.9 ± 0.4
10	20.2 ± 1.6	515.0 ± 68.5	29.8 ± 3.3	4.2 ± 0.4
20	20 ^a	16 ^a	-	-
30	15 ^a	25 ^a	-	-
30	4 ^b	20 ^b	-	-
40	2.5 ^b	22 ^b	-	-
TEC				
0.1	-	-	-	5.6 ^c
0.2	-	-	-	7.4 ^c
0.3	-	-	-	6.9 ^c
1	93.3 ± 30.4	12.8 ± 1.5	47.2 ± 5.5	8.7 ± 1.2
3	54.4 ± 11.3	21.3 ± 4.8	57.0 ± 7.8	11.3 ± 2.0
5	33.5 ± 2.4	529.2 ± 68.5	48.5 ± 7.9	6.0 ± 0.9
10	31.2 ± 3.2	468.5 ± 62.2	37.6 ± 3.2	9.0 ± 0.9
20	-	-	22.5 ^d	2.0 ^d
30	-	-	17.5 ^d	3.2 ^d
TBAC				
0.1	-	-	-	6.1 ^e
0.2	-	-	-	8.5 ^e
0.3	-	-	-	9.7 ^e
1	62.9 ± 5.7	32.7 ± 2.0	69.1 ± 14.8	4.8 ± 0.7
3	55.5 ± 4.7	25.1 ± 2.7	61.1 ± 12.9	11.9 ± 1.8
5	59.9 ± 6.5	15.7 ± 2.9	56.2 ± 7.7	5.3 ± 0.6
10	45.4 ± 4.0	570.7 ± 96.4	40.8 ± 5.1	6.1 ± 0.5

^a by Zhang et al., 2012, solution casting [23];^b by Darabian et al., 2020, solution casting [24];^c by Umemura et al., 2021, solution casting [25];^d by Žiganova et al., 2023, hot pressing [26];^e by Wang et al., 2008, solution casting [27].

A decrease in the tensile strength and an increase in elongation at break of PLA films with an increase in the amount of a plasticizer were also confirmed in other studies [28]. Darabian et al. (2020) demonstrated that the addition of TA to PLA (90 kDa) in the amounts of more than 30 and 40 wt.% resulted in a decrease in the tensile strength of the films and in an increase in elongation up to 20–30% [24]. In the study by Zhang et al. (2012), adding 5–40 wt.% TA to solution-cast PLA films increased elasticity by up to 25% but decreased tensile strength from 30 to 10 MPa [23]. The differences in the absolute mechanical values (despite similar trends) can be attributed primarily to their distinct molecular weights.

Other authors [29] observed that the addition of TA and PEG led to a decrease in tensile strength and to an increase in elasticity of PLA films. With the addition of TA in the amount from 10 wt.% to 30 wt.%, tensile strength of the films decreased from 32.5 MPa to 10 MPa, and elongation increased from 5.4% to 81.0%. This effect of TA in PLA films is attributed to enhanced polymer chain mobili-

ty. This leads to an increase in the film's elasticity and to a greater distance between polymer chains due to the addition of the plasticizer. Overall, this results in a decrease in intermolecular interactions and, consequently, in tensile strength. [15, 30, 31].

At the same time, a number of studies have shown that in some cases, the addition of plasticizers can increase tensile strength. For example, a combination of triacetin and polyethylene glycol resulted in increased strength in acrylic resin [32]. Increased tensile strength is known for chitosan-starch mixtures with the addition of 1.5% glycerol [33]. A similar effect is known for TBAC when added to polyvinyl chloride [34]. In contrast to TA, a small amount of TEC (1 wt.%) slightly increased the tensile strength of PLA to 93 MPa but reduced the elongation at break to 12%. At higher concentrations (5 and 10 wt.%), however, tensile strength decreased while elongation surged dramatically to 529%. Although TA and TEC interact similarly with PLA through polar interactions between ester groups—and show good compatibility with it—TEC may

enable greater deformation due to its ethyl groups. This is supported by the cracks seen in SEM images of PLA/TEC films. In the other study it is shown that when soaking a PLA film with TEC or adding TEC to PLA during melting, the tensile strength drops from 31 MPa to 11 MPa, while elongation at break increases from 23% to 216% [35].

When TBAC was added to PLA films in low concentrations (1 wt.% and 3 wt.%), the tensile strength maintained at the level of 55–62 MPa and elongation at break increased to 25–32%. The addition of 5 wt.% of TBAC to PLA film led to a decrease in the elongation at break to 15%. With a 10 wt.% concentration of TBAC in the PLA film, the tensile strength decreased down to 45 MPa, whereas the elongation at break significantly increased up to 570%.

A clear dependence of mechanical properties on plasticizer concentration was also evident for PHB films. The introduction of TA into PHB films significantly increased the tensile strength, to 65 MPa and 81 MPa at 1 wt.% and 3 wt.% TA, respectively. However, the elongation at break reached 8% at 1 wt.% TA but then decreased slightly to 6% at 3 wt.%. Increasing the TA content in PHB films reduced both property values by a factor of 1.5 compared to neat PHB. This effect occurs because TA, when added at high concentration, can act as a solvent for the polymer, which was previously reported in the literature [36, 37]. The addition of 1 wt.% and 3 wt.% TEC to PHB films increased the tensile strength to 47 MPa and 57 MPa, respectively, and raised the elongation at break to 8–10%. At 5 wt.% TEC, both mechanical properties showed a slight decline relative to the films with 1 wt.% and 3 wt.% TEC. Nevertheless, they remained superior to those of the neat PHB film. Increasing the TEC content in PHB films to 10 wt.% reduced the tensile strength relative to neat PHB but significantly enhanced the elongation at break. The change in tensile properties also correlated with the amount of TBAC added. At 10 wt.% TBAC, the tensile strength dropped to 40 MPa. In contrast, the elongation at break remained largely unchanged across all tested plasticizer concentrations.

Conventionally used for film production, low-density polyethylene (LDPE) is characterized by a tensile strength of approximately 10–17 MPa and an elongation at break of at least 200% and often above 500%. [38]. For polypropylene (PP), these properties fall within the ranges of 30–50 MPa for tensile strength and 200–700% for elongation at break [39]. At low plasticizer concentrations (1–3 wt.%), TBAC imparted the highest elongation at break to PLA while maintaining tensile strength close to that of neat PLA. However, to achieve elasticity comparable to that of polyolefins, a much higher plasticizer loading (5–10 wt.%) of any of the studied compounds was required.

The following compositions were selected for subsequent testing in model solutions: PLA with 10 wt.% TA, PLA with 3 wt.% TEC, PLA with 1 wt.% TBAC, PHB with 1 wt.% TA, PHB with 3 wt.% TEC, and PHB with 3 wt.%

TBAC. This selection was based on their optimal balance of properties, aligning with relevant standards for biodegradable polymers [21]. According to the standard, PLA-based films must have a tensile strength >50 MPa and an elongation at break >5%. For PHB-based films, the required minimum values are >25 MPa and >26%, respectively.

3.3. FT-IR analysis of pure and plasticized PLA and PHB films

The infrared (IR) spectrum of the semicrystalline P(3HB) displayed at least two main bands, which were generated by the “crystalline” and “amorphous” regions. The absorption band at 1721–1724 cm^{-1} , attributed to carbonyl (C=O) stretching vibrations, is characteristic of the crystalline phase. In contrast, the other bands, such as the one near 1182 cm^{-1} , are predominantly associated with the amorphous regions of the polymer (Figure 3a). FTIR analysis of the PLA spectrum showed intense ester group vibrations between 1250 and 1050 cm^{-1} , with characteristic peak at 1170–1200 cm^{-1} (for propionic acid esters) and 1060–1120 cm^{-1} (for secondary alcohol esters) (Figure 3b). Additional bands at 1440–1460 cm^{-1} and 1375–1385 cm^{-1} corresponded to deformation vibrations of methylene and methyl groups, respectively.

The IR spectra of triethyl citrate (TEC) and triacetin (TA) exhibited characteristic bands of ester functional groups. A strong carbonyl (C=O) stretching vibration appeared at ~1737 cm^{-1} for TA and between 1735–1750 cm^{-1} for TEC. Both spectra also showed C–O ester bond vibrations between 1100–1300 cm^{-1} and C–H stretching bands from 2800–3000 cm^{-1} , consistent with their alkyl chain structures.

The IR spectrum of tributyl-o-acetyl citrate (TBAC) showed characteristic ester peaks: a strong C=O stretch at ~1740–1760 cm^{-1} , along with C–O and C–H stretches from its ester and aliphatic groups. In the presented spectra, the overlapping bands of the plasticizers and polymers confirm their close molecular contact. Shifts and changes in peak intensity, especially in the carbonyl region, indicate the presence of electronic interaction between the components. The more pronounced changes in the PLA spectra compared to PHB indirectly indicate stronger (possibly hydrogen) bonding of the plasticizers with the PLA matrix, which correlates with the more significant improvement in PLA elasticity compared to PHB observed in the study. The relative stability of the main peak positions upon plasticization with TBAC is consistent with its role as a more inert, bulkier plasticizer.

3.4. TGA of pure and plasticized PLA and PHB films

The introduction of plasticizers into a polymer matrix commonly shifts its melting and degradation temperatures, as confirmed by our data. Thermograms of PLA/TA 10 wt.%, PLA/TEC 3 wt.%, PLA/TBAC 1 wt.%, PHB/TA 1wt.%, PHB/TEC 3 wt.%, and PHB/TBAC 3 wt.% are shown in Figures 4 and 5.

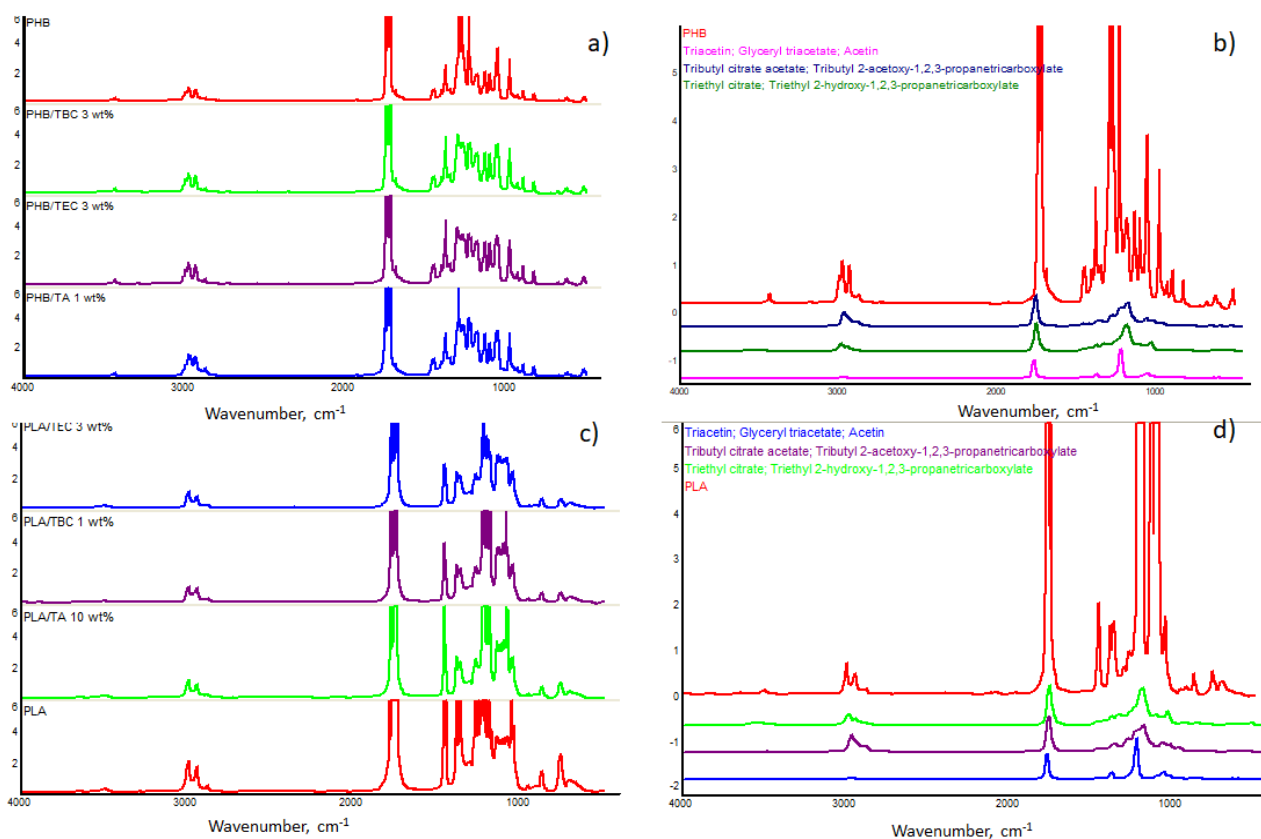


Figure 3 IR spectra of film samples: PHB, PHB/TA 1 wt.%, PHB/TEC 3 wt.%, and PHB/TBAC 3 wt.% (a, b); PLA, PLA/TA 10 wt.%, PLA/TEC 3wt.% and PLA/TBAC 1 wt.% (c, d).

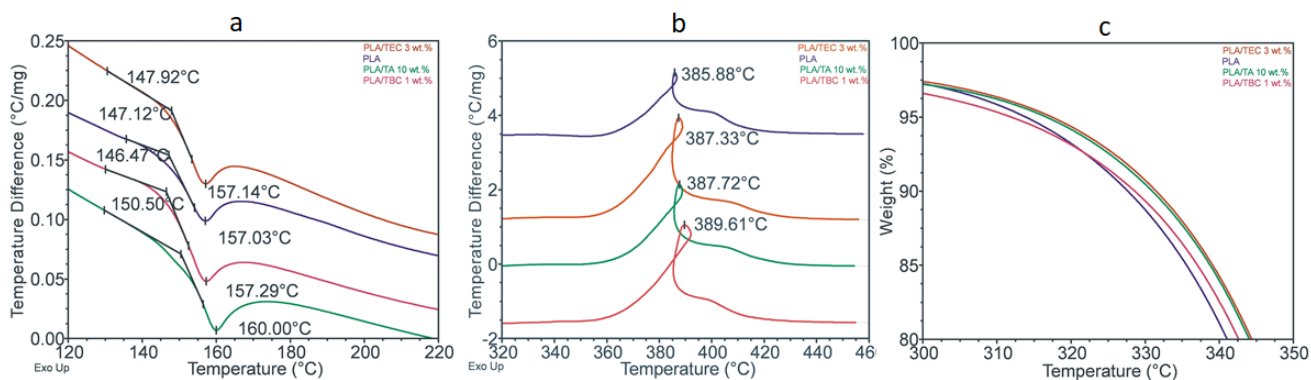


Figure 4 Thermograms of PLA, PLA/TA 10 wt.%, PLA/TEC 3 wt.%, and PLA/TBAC 1 wt.% films: melting temperature (DSC) (a), degradation temperature (DSC) (b), dependence of weight loss on degradation temperature (TGA) (c).

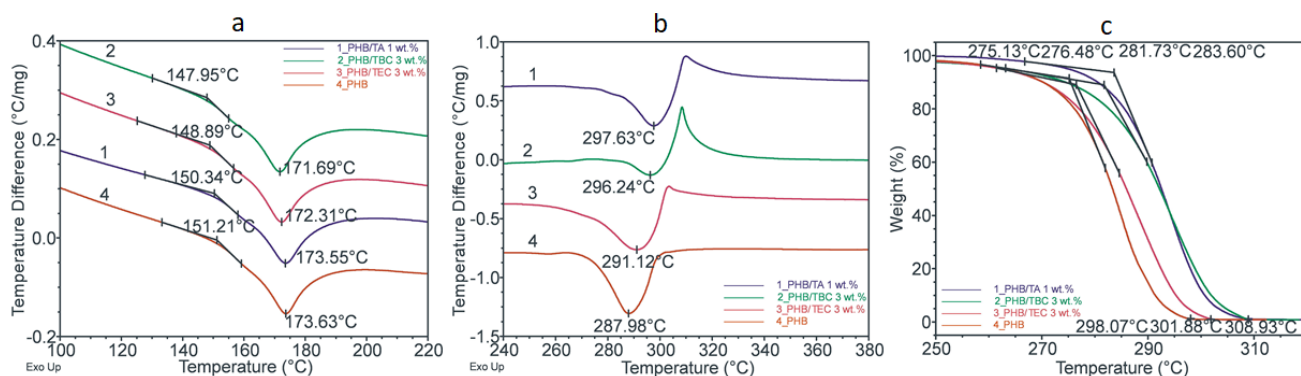


Figure 5 Thermograms of PHB, PHB/TA 1 wt.%, PHB/TEC 3 wt.%, and PHB/TBAC 3 wt.% films: a - melting temperature (DSC), b - degradation temperature (DSC), c - dependence of weight loss on degradation temperature (TGA).

It can be noted that addition of TEC 3 wt.% and TBAC 1 wt.% in PLA films had virtually no effect on melting onset temperature and melting peak, while the addition of TA 10 wt.% led to an increase in temperature by 3–4 °C. This was also observed for degradation temperature and degradation rate (Figure 4a,c). The original PLA exhibited a 17% weight loss at 340 °C and fully degraded at 385.88 °C (Figure 4b). Thermal degradation of the plasticized films was slower: a similar weight loss (17%) for PLA/TA 10 wt.% and PLA/TEC 3 wt.% films was recorded at 346 °C. The degradation temperature of PLA increased by 2 °C with the addition of 3 wt.% TEC or 10 wt.% TA, and by 4 °C with 1 wt.% TBAC.

In contrast to PLA, the melting temperatures of PHB films decreased in all cases upon plasticizer addition. For PHB/TA 1 wt.%, PHB/TEC 3 wt.%, and PHB/TBAC 3 wt.% films, T_m was 173.55 °C, 172.31 °C, and 171.69 °C, respectively (Figure 5). The onsets of the melting temperature peaks were also shifted toward lower temperatures, which could influence the material's processability by various methods. Plasticizer addition raised the degradation temperature of PHB significantly, by up to 10 °C. The maximum degradation temperature values were recorded for the PHB/TA 1 wt.% film.

The type of plasticizer influenced the thermal stability of PHB films. The temperature of complete degradation shifted to 301 °C with 3 wt.% TEC, and to a higher 308 °C with either 1 wt.% TA or 3 wt.% TBAC.

3.5. Effect of incubation in different model solutions on the mechanical properties of films

According to the results of incubation of PLA films in model solutions, a decrease in mechanical properties was observed for almost all film samples of all compositions, regardless of the model solution, except for the pure PLA film, whose tensile strength remained relatively at the same level.

A significant reduction in elongation at break (by a factor of 2–8) was observed for all plasticized films after 1 and 3 days of incubation. Despite this drop from their original levels, the values generally satisfied the standard requirement of >5% for biodegradable PLA. The only exception was the PLA film with 3 wt.% TEC incubated in the lactic acid solution (Figure 6).

Meanwhile, the highest elongation at break value was still observed for PLA/TA films, ranging from 133.4% to 337.4% after 1 day and from 123% to 235% after 3 days depending on the solution, whereas PLA films with 1 wt.% TBAC and 3 wt.% TEC showed significantly lower values. However, the same was true for the initial films before incubation.

By day 10, the elongation at break of PLA films with 3 wt.% TEC had fallen below the required 5% after incubation in distilled water, citric acid, and lactic acid. In contrast, films incubated in the sodium chloride solution

maintained a high elongation at break of 26.4%, well above the required 5% minimum. For the other plasticized films, this value still remained within the required range. However, the tensile strength of all the plasticized films dropped below the 50 MPa requirement after just one day of incubation in any solution and continued to decline throughout the storage period (Figure 6).

The PHB films exhibited a more rapid decline in properties (Figure 7). After just one day in distilled water or lactic acid, both tensile strength and elongation at break had already fallen below the standard requirements for PHB (<25 MPa and <26%, respectively). This deterioration progressed steadily until the end of the incubation period. In the citric acid solution, an acceptable tensile strength was recorded for the neat PHB film (35.6 MPa) after one day of incubation. On day 3, acceptable values were observed for PHB films with 1 wt.% TA (37.6 MPa) and 3 wt.% TEC (28.8 MPa). By day 10, the films retaining acceptable strength were those with 3 wt.% TEC (30.9 MPa) and 3 wt.% TBAC (22.6 MPa). After 3 and 10 days in lactic acid, the highest tensile strength was recorded for neat PHB (31.1 MPa at both time points). In the sodium chloride solution, however, the PHB film with 3 wt.% TBAC performed best, with strengths of 31.2 MPa (day 3) and 25.2 MPa (day 10).

In general, plasticizing PHB proved ineffective. While TA addition improved elongation at break, it did not address the low tensile strength. Conversely, TEC and TBAC enhanced tensile strength but had no significant effect on elongation.

For PLA, all plasticizers markedly enhanced both elongation at break and tensile strength. In some instances, the improvement was dramatic—for example, adding 10 wt.% TA caused a 33-fold increase in elongation, which may even be excessive. However, after incubation in various solutions, these values dropped dramatically. Despite this, PLA films plasticized with TA or TBAC still exhibited acceptable elongation at break after 10 days in all solutions. Their tensile strength, however, had fallen to between 10 and 40 MPa, which is below the 50 MPa requirement.

3.6. Migration of plasticizers into model solutions

For subsequent investigations, PLA films plasticized with 1 wt.% TBAC were selected. This selection was based on several factors. First, the films exhibited favorable mechanical properties: tensile strength was maintained near the level of neat PLA while elongation at break increased to over 30%. Second, the required plasticizer content was low (1 wt.%), minimizing potential migration into food. Finally, published data indicate that TBAC can accelerate the biodegradation of both PLA and PHB [40].

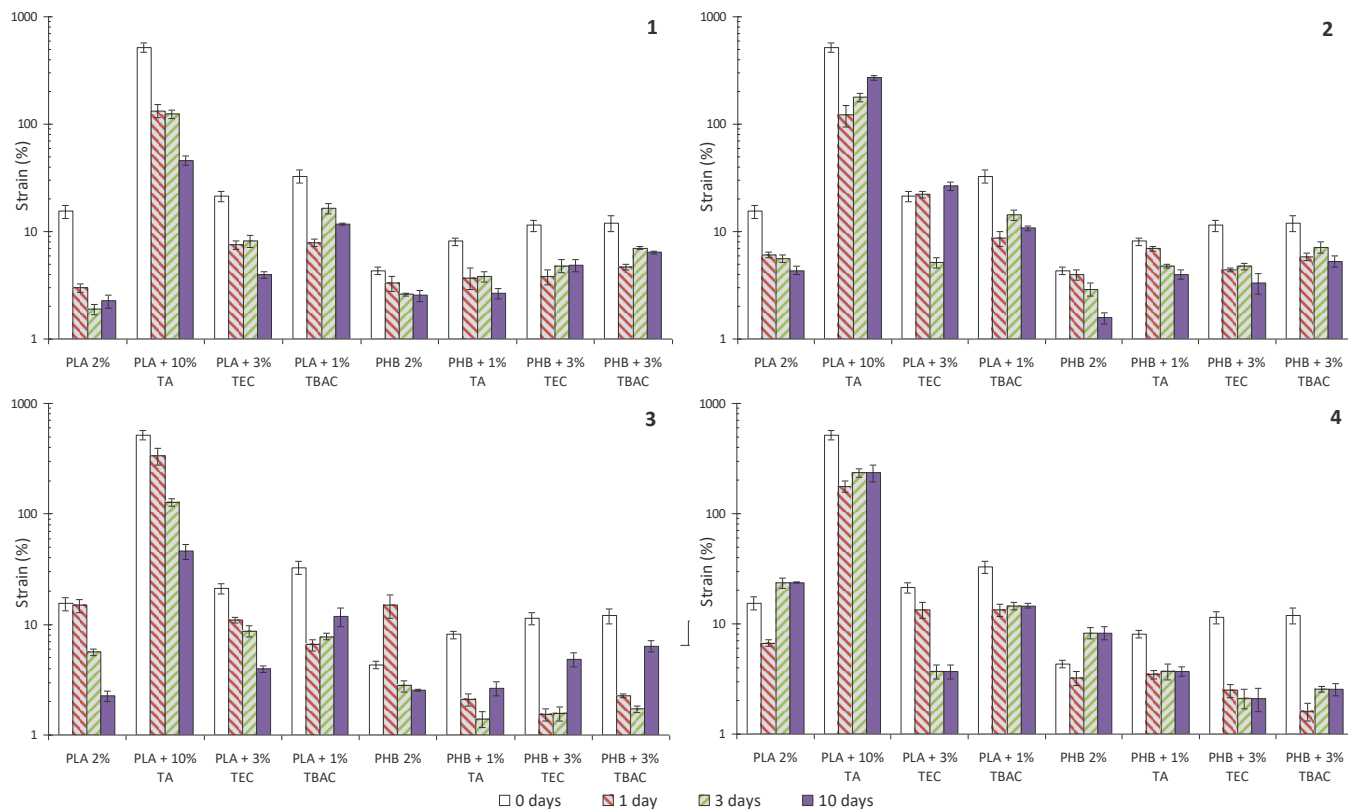


Figure 6 Change in elongation at break of pure and plasticized PLA and PHB films after incubation in model solutions: 1 – distilled water, 2 – sodium chloride solution, 3 – citric acid solution, 4 – lactic acid solution.

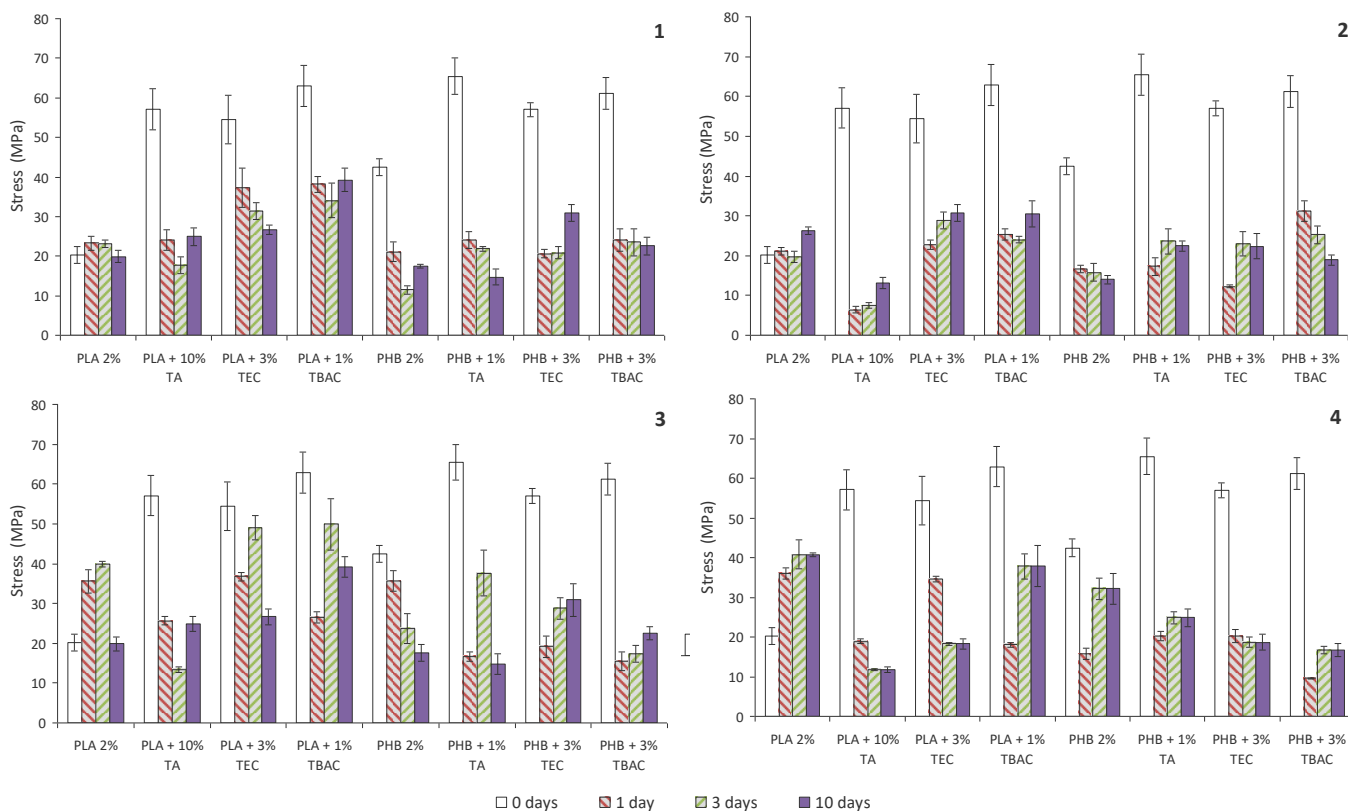


Figure 7 Change in tensile strength of pure and plasticized PLA and PHB films after incubation in model solutions: 1 – distilled water, 2 – sodium chloride solution, 3 – citric acid solution, 4 – lactic acid solution.

To assess the stability of plasticized films in aqueous solutions, PLA films containing 1 wt.% TBAC were incubated for 10 days in distilled water, and aqueous solutions of lactic acid, citric acid, and sodium chloride (Figure 8). Analysis of residual content of plasticizer showed its greatest loss of 35% after incubation in citric acid. However, incubation in distilled water and lactic acid solution resulted in a lower TBAC loss of 32% and 23%, respectively. The lowest plasticizer loss, 11%, was noted during storage of films in a sodium chloride solution.

Migration process depends on molar mass, chemical nature and amount of the plasticizer, the polarity of the molecules, the plasticization process, and the homogeneity of the compound and the surrounding environment, temperature, contact area and other conditions. Plasticizers migration was described in the study by Eva Hernández-García, where PHBV films modified with triglycidyl isocyanurate and dicumyl peroxide were incubated in a 10% ethanol solution and in vegetable oil, and the resulting migration was $2.7 \text{ mg}\cdot\text{dm}^{-2}$ [41]. According to Li et al. [42], the migration of rosin from cellulose nanocrystal-grafted PHBV films (CNC-R) into a 10% ethanol solution and into isooctane reached $161.5 \text{ }\mu\text{g}/\text{kg}$.

The potential of polyvinylidene chloride/polyvinyl chloride food film containing TBAC for the storage of cod and herring was studied by Zygoura et al. [43]. It was found that the final TBAC concentrations in cod fillets ranged from 11.1 to 12.8 mg/kg, while the corresponding values for herring samples ranged from 32.4 to 33.4 mg/kg. The authors concluded that the fat content of the stored fish fillets significantly affected the migration of TBAC. It is worth noting, that the obtained values of plasticizers migration did not exceed the permissible daily intake ($1.0 \text{ mg}/\text{kg}$ body weight) established for TBAC [44].

Incubation of the plasticized films in aqueous solutions demonstrated some dependence of TBAC migration on the pH of the solution. Although TBAC itself is not hydrolyzed, the acidic conditions (low pH) of the citric and lactic acid solutions may promote hydrolysis of the PLA film. This degradation of the polymer would, in turn, increase plasticizer diffusion rates. The degradation of PLA proceeds at a higher rate under acidic conditions than at neutral pH [45]. Consequently, the residual plasticizer content in the film was lower after incubation in the acidic solutions than in the salt solution.

3.7. Chicken fillet storage in plasticized biodegradable films

According to the results of microbial contamination study, the obtained experimental films had an inhibitory effect on microorganisms. This was indicated by the differences in microbial contamination of chicken fillet stored for a week (Table 2).

The initial microbial contamination of the fillet was acceptable ($<10^4$ CFU/g on PCA and Endo media, but

10^5 CFU/g on MRS medium). By day 3 of storage, microbial counts had increased. Compared to the control (PE film): neat PLA film showed similar contamination levels on PCA and Endo media, but a two-order-of-magnitude higher count on MRS medium; PLA/TBAC film exhibited a one-order-of-magnitude higher count on PCA, a one-order-of-magnitude lower count on Endo medium, and a two-order-of-magnitude higher count on MRS medium.

On day 7, an increase in microbial contamination was observed for all the samples. The greatest contamination was noted for control samples in PE films, where CFU/g value on PCA medium reached $1.19\cdot 10^7$ CFU/g, while for all PLA-based films this value was two-order-of-magnitude below.

For Endo agar, the contamination trend was similar for both control samples and the one stored in pure PLA film, whereas it was one-order-of-magnitude below for the samples stored in PLA/TBAC films.

For MRS agar, the contamination value was similar for the control samples and one order of magnitude higher for the samples stored in pure PLA film and PLA/TBAC film. Thus, the control samples were more contaminated than the one stored in the obtained experimental PLA films.

This study did not employ dedicated antibacterial additives. Instead, we relied solely on plasticizers (TA, TEC, and TBAC), which have been reported to exhibit such properties [46,47,48].

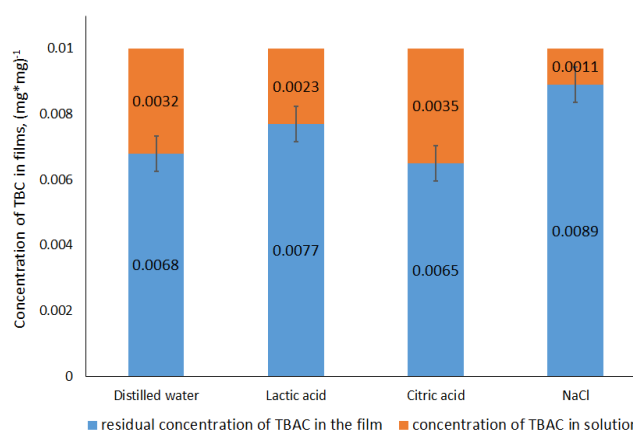


Figure 8 Residual TBAC content in PLA/TBAC 1 wt.% film after 10-days incubation in various aqueous solutions.

Table 2 Microbial contamination of chicken fillet samples after their storage in plasticized biodegradable films (in CFU/g).

Film sample	Media	Time	
		3 days	7 days
PE (control)	PCA	$(3.33 \pm 4.08) \cdot 10^3$	$(1.19 \pm 0.08) \cdot 10^7$
	Endo agar	$(1.07 \pm 1.25) \cdot 10^5$	$(5.23 \pm 1.50) \cdot 10^6$
	MRS	$(4.65 \pm 1.58) \cdot 10^3$	$(1.48 \pm 4.58) \cdot 10^6$
PLA/TBAC	PCA	$(1.83 \pm 2.25) \cdot 10^4$	$(3.03 \pm 0.37) \cdot 10^5$
	Endo agar	$(4.00 \pm 1.41) \cdot 10^4$	$(1.87 \pm 1.00) \cdot 10^5$
	MRS	$(8.27 \pm 3.50) \cdot 10^5$	$(2.87 \pm 0.16) \cdot 10^7$
PLA	PCA	$(3.33 \pm 4.08) \cdot 10^3$	$(6.33 \pm 0.89) \cdot 10^5$
	Endo agar	$(2.20 \pm 2.48) \cdot 10^5$	$(2.75 \pm 0.67) \cdot 10^6$
	MRS	$(1.60 \pm 0.43) \cdot 10^5$	$(2.72 \pm 0.03) \cdot 10^7$

Acetyl tributyl citrate has been reported to exhibit moderate antibacterial activity against *Klebsiella pneumoniae*, *Pseudomonas aeruginosa*, and *Staphylococcus aureus*. [48]. We hypothesize that the observed antibacterial effect is due to the presence of the plasticizer in the film and its subsequent gradual release into the environment. Another potential antimicrobial mechanism is the low oxygen permeability of PLA films compared to polyethylene, which can inhibit the growth of aerobic bacteria [49].

There is a large amount of evidence that the addition of various essential oils or metal oxides increases the shelf life of food and prevents the development of pathogenic microflora. Similarly, Heydari-Majd et al. [50] reported that both pure PLA films inhibited microbial activity on fresh fish fillets, albeit slightly less effectively than PLA films containing peppermint or Shirazi thyme essential oils. The authors attribute this to the air impermeability of PLA films, which inhibits the growth of aerobic microflora. Interestingly, PLA films showed no antimicrobial activity in antimicrobial tests against *Escherichia coli*, *Salmonella enterica*, *Pseudomonas aeruginosa*, *Bacillus cereus* and *Staphylococcus aureus* [50]. Javidi et al. (2016) also demonstrated the antimicrobial activity of PLA films deposited with oregano essential oil. *S. aureus* showed the highest sensitivity, while *E. coli* was the most resistant. Evaluation of microbial growth on rainbow trout fillets showed that PLA-based films with oregano essential oil inhibited microbial growth. This inhibitory effect was maintained for 16 days, contributing to an extended shelf life of the chilled trout [51]. Zhao et al. (2025) developed a multifunctional antimicrobial PLA-based covering material. Polyhexamethylene guanidine hydrochloride (PHMG) was introduced as the antimicrobial additive of the film. The resulting film was effective in preventing microbial growth when used as antibacterial packaging for poultry products, extending the shelf life of fresh chicken breast up to eight days [52]. In the study by Wang et al. (2022), a cinnamic aldehyde-loaded PLA/PBAT film effectively in-

hibited the growth of *E. coli* and *S. aureus* at 4 °C. By the 10th day, it resulted in average reductions of 3.6 and 4.1 log CFU/g for *E. coli* and *S. aureus*, respectively [53]. Therefore, incorporating essential oils into PLA films presents a promising strategy to enhance their antimicrobial efficacy and improve food preservation, as supported by both the literature and the findings of this study.

Evaluation of organoleptic parameters by three independent experts revealed that storing chicken fillets in the experimental PLA films slightly improved the product's sensory characteristics during long-term storage (Table 3).

On day 3, the samples stored in the experimental PLA films scored, on average, 0.2–0.6 units higher on the organoleptic scale than the control sample. A difference in color and consistency was particularly evident. Specifically, control samples stored in PE films developed a yellowish tint and noticeable stickiness compared to those stored in the experimental PLA films (Figure 9).

By day 7, the samples stored in the experimental PLA films scored, on average, 0.4–2.0 units lower on the organoleptic scale than the samples stored in PE film. The greatest difference was in the smell and color of the samples. The unpleasant odor of spoiled meat was very pronounced in the samples stored in PE film. In contrast, the odor was less pungent and generally weaker in the samples stored in the experimental PLA films. As for the color, the yellowness of the samples decreased in the series PE>PLA>PLA/TBAC>PLA.

HPLC analysis of chloroform extracts from the fillet slices showed a residual plasticizer concentration of $2.10 \pm 0.03 \mu\text{g/g}$ on day 3 of the experiment. The measured concentration is well below the Specific Migration Limit (SML) set by the European Food Safety Authority (EFSA), which stipulates that the overall migration of all substances must not exceed 60 mg per kg of food or 10 mg per dm^2 of contact material [54]. For the fillet slices incubated for 7 days no plasticizer was determined.

Table 3 Results of organoleptic parameters evaluation of chicken fillet samples after their storage in plasticized biodegradable films (the average scores of three independent experts are given).

Characteristic	Material	Control	3 days	7 days
General appearance	PE	5.0	4.7	2.3
	PLA		4.7	3.0
	PLA/TBAC		5.0	3.3
Color	PE	5.0	4.0	2.3
	PLA		4.7	2.7
	PLA/TBAC		4.0	3.7
Smell	PE	5.0	3.7	1.7
	PLA		4.3	2.3
	PLA/TBAC		3.7	2.7

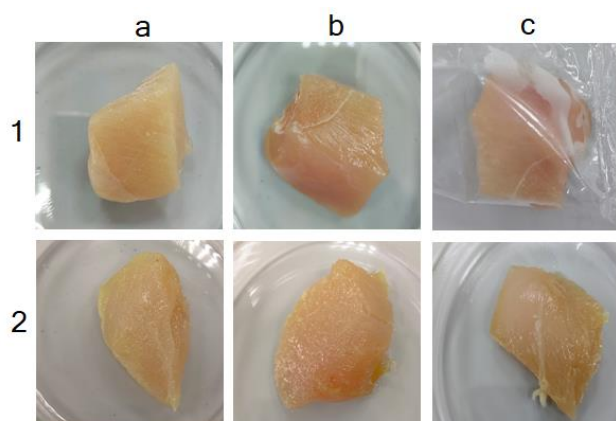


Figure 9 The general appearance of chicken fillet samples after their storage in plasticized biodegradable films: 1 – on the 3rd day, 2 – on the 7th day; a – stored in PE film, b – stored in PLA film, c – stored in PLA/TBAC film.

Previously, Muñoz-Pabon et al. (2023) studied the sensory characteristics of pork mince stored in PLA-based biocomposite films using nisin and oregano oil as active antimicrobial components. During storage, the hardness and stickiness of the meat changed significantly in the biocomposite without active components. In contrast, the biocomposite containing active components showed no significant changes in the meat's texture or color over 21 days. According to the authors, this demonstrates the benefit of using PLA for improving stored meat quality. In our study, long-term storage of fillet samples in the biodegradable films resulted in a slight improvement of their sensory properties. The comparative analysis with food-grade PE film indicates that such biodegradable films represent a promising and viable alternative to traditional packaging [55].

4. Limitations

The biodegradability of the developed films was not assessed in this work. The biodegradability of polylactide (PLA) [56] and poly-3-hydroxybutyrate [57] is well-documented, although its rate is highly dependent on environmental conditions and can be suppressed by low temperature or humidity. Plasticizer additives generally accelerate biodegradation [58]. This effect is also known for PLA and PHB films plasticized with TBAC [40].

The bubble-point pressure method provides a limited assessment of porosity. It only detects pores that form continuous channels through the entire film thickness, meaning it cannot register closed or dead-end pores. Furthermore, the method fails to detect through-pores with diameters below approximately 20 nm and cannot quantify the proportion, size distribution, or total volume of such open porosity.

Due to the extensive scope of the required microbiological analysis, only the PLA/TBAC 1% films were selected

for the chicken fillet storage experiments. This choice was based on their suitable mechanical properties and relatively low plasticizer content. We suggest that other plasticized film formulations could also be viable for food packaging, although this requires confirmation through further research.

5. Conclusions

In this work, we obtained and studied PLA- and PHB-based films plasticized with TA, TEC, and TBAC. The introduction of TA and TEC affected the film surface, leading to the formation of pores and cavities. In contrast, TBAC had no noticeable effect on the surface morphology. Plasticization of PLA resulted a substantial increase in elongation at break (up to 30-fold). For PHB films, the same mechanical properties changed to a lesser extent upon plasticization. The plasticized films exhibited lower crystallization and melting temperatures compared to the non-plasticized films. Following incubation in aqueous model solutions, the plasticized films exhibited gradual migration of the plasticizers into the environment, accompanied by a moderate decline in their mechanical properties. The plasticized films exhibited an antimicrobial effect, which successfully extended the shelf life of a model meat product (chicken fillet) by up to one week.

Supplementary materials

No supplementary materials are available.

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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None.

Author contributions

Conceptualization: A.A.S.
 Methodology: A.A.S.
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 Formal analysis: N.L.E., K.E.Z., S.N.S., N.D.D.
 Investigation: N.L.E., K.E.Z., A.N.B., S.N.S., E.N.T., N.D.D., A.S.S.
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 Writing—original draft preparation: A.A.S., N.L.E., K.E.Z., A.N.B.
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Conflict of interest

The authors declare no conflict of interest.

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