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Assessment of IAS and NIAS in Plasma-Treated Biopolymer Films: Implications for Food Packaging Safety and Quality

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Abstract

Biopolymers are increasingly explored as safer and more sustainable food packaging materials. This study evaluated the migration behavior of intentionally and non-intentionally added substances (IAS and NIAS), as well as the safety of gelatin and xanthan gum blends reinforced with microcrystalline cellulose, with and without oxygen plasma treatment, incorporating glycerol and limonene as plasticizers. Migration tests were conducted according to European Union (EU) Regulation No. 10/2011 using simulants of different polarities, and IAS/NIAS were analyzed by gas chromatography–mass spectrometry and ultra-high-pressure liquid chromatography–quadrupole time-of-flight mass spectrometry (GC–MS and UPLC-QTOF-MS). Films containing limonene were also evaluated for antioxidant activity. Results showed that plasticizer migration is strongly influenced by simulant polarity, glycerol predominantly migrated into hydrophilic media, whereas limonene and its derivatives exhibited higher migration in fatty simulants. Ethanol 95% acted as a conservative worst-case simulant, promoting extensive migration, while substantially lower migration levels were observed in isooctane and tenax plasma treatment resulted in modest changes in volatile compound migration, while significantly enhancing the antioxidant activity of limonene-containing films. Although overall migration levels were low under most of the tested conditions, NIAS formation, particularly from limonene degradation, highlights the need to account for chemical stability and simulant type when assessing bio-based films. Overall, the study demonstrates that film composition, surface modification, and simulant characteristics jointly influence migration behavior and functional performance under the evaluated conditions reinforcing the need to adapt current regulatory frameworks to the specific behavior of biopolymeric packaging materials.

Keywords: biopolymer films; food packaging migration; IAS/NIAS analysis; oxygen plasma treatment; limonene plasticizer

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1. Introduction

Increasing pressures driven by environmental and regulatory concerns are pushing the packaging industry towards the incorporation of sustainable materials into the production of new products [1]. Biopolymers obtained from renewable feedstocks have attracted

growing attention as potential substitutes, owing to their biodegradability, reduced carbon footprint, and capacity to meet the performance requirements of food packaging [2].

Among the wide range of available biopolymers, polysaccharides and proteins stand out due to their film-forming capacity, biocompatibility, renewability, and biodegradability [3]. Gelatin, a protein derived from partial hydrolysis of collagen from animal skin and bones, is abundant and inexpensive [4,5]. It forms transparent films with low oxygen permeability and water solubility but is brittle and lacks flexibility and strength [1,3]. These drawbacks can be mitigated by combining gelatin with other polymers to obtain improved materials. Among the various biopolymer candidates, xanthan gum (XG), a heteropolysaccharide composed of repeating pentasaccharide units (two glucose, two mannoses, and one glucuronic acid), is produced by the Gram-negative bacterium Xanthomonas campestris. It is biodegradable, biocompatible, and non-toxic, which supports its extensive use in the food and pharmaceutical industries, as well as in research for innovative products [6–8]. Cellulose, one of the most abundant natural polymers, consists of repeating β-D-glucose units with three free hydroxyl groups per monomer [5,8]. According to Pereira et al. [3], cellulose serves as an excellent reinforcing polymer in gelatin–xanthan gum films, providing strength and water resistance.

A key limitation of biopolymers in packaging lies in their inferior mechanical performance and processing challenges compared to conventional plastics, which can be partially overcome using plasticizers [9]. The use of plasticizers helps to address these issues by reducing intermolecular forces, increasing flexibility, and improving processability and mechanical properties [9,10]. Glycerol, a by-product of biodiesel production, is one of the most used plasticizers due to its high availability and the presence of three hydroxyl groups, which enhance interactions with polymer chains, imparting elasticity and softness [10,11]. Alternatively, limonene is a natural terpene obtained from citrus industry waste. Besides acting as a green plasticizer, it can improve water vapor and oxygen barrier properties and confer antimicrobial and antioxidant functionalities to biopolymeric films [12–15]. These antioxidant effects may be further enhanced by applying plasma etching to the film surface, owing to the reactive species generated.

Plasma etching is a clean, fast, and environmentally friendly technique to modify the surface properties of polymers [16]. Two main effects can occur: (i) superficial material removal through ion bombardment or energetic species, altering surface nanoroughness [17], and (ii) introduction of specific functional groups, depending on the plasma composition, thus modifying surface chemistry [18–20]. In addition, plasma-induced crosslinking, especially in proteins, can further enhance barrier properties, making these materials attractive for food packaging [21]. However, in addition to improving surface properties, plasma treatment may also alter the mobility of small molecules in the polymer matrix, which could influence the migration of certain substances [17–19,21].

An important but often overlooked issue in biopolymers is the migration of intentionally added substances (IAS) and non-intentionally added substances (NIAS) into food. IAS may result from synthesis residues (e.g., sodium hydroxide) or additives used to improve processing (e.g., oxidation catalysts) [22]. NIAS, in contrast, can derive from polymer degradation, additives, or reactions between them, and even from plasma modification. In petroleum-based plastics, the migration of IAS and NIAS has been extensively investigated due to potential toxicological concerns and regulatory requirements. In contrast, despite the increasing use of biopolymeric materials, studies addressing IAS and NIAS migration in these systems remain scarce [23,24]. This gap highlights a critical need to better understand the chemical safety of bio-based packaging materials under realistic processing and application conditions.

As highlighted by Kato et al. [24], although the use of biopolymeric materials has grown significantly, studies concerning their chemical safety and potential migration into foods remain limited. In this context, this work focused on investigating whether the incorporation of different plasticizers, glycerol and limonene, into films of gelatin/xanthan gum reinforced with microcrystalline cellulose, combined with oxygen plasma treatment, results in distinct migration patterns of IAS and NIAS under different food simulant conditions, and whether plasma exposure may influence migration behavior while enhancing the functional performance of limonene. By combining migration assessment, NIAS screening, and antioxidant evaluation, this integrated approach provides new insights into the safety performance balance of plasma-treated biopolymeric films for food packaging applications within the scope of the experimental conditions evaluated and contributes to advancing regulatory and safety assessments for sustainable materials. This work provides a focused assessment of migration behavior, NIAS formation, and functional performance in plasma-treated biopolymer films, with particular emphasis on the influence of food simulant selection.

2. Materials and Methods

2.1. Reagents and Materials

Gelatin, xanthan gum, microcrystalline cellulose, and glycerol were purchased from Êxodo Científica (Sao Paulo, Brazil). Ethanol, isooctane and acetic acid of 99% purity, supplied by Scharlau Chemie S.A. (Barcelona, Spain), and ultrapure water were used. Glycerol (CAS 56-81-5), β-Pinene (CAS 127-91-3), Limonene (CAS 5989-27-5), Geraniol (CAS 106-24-1), ϒ-Terpinene (CAS 99-85-4), Citronelol (CAS 106-22-9), 1-Nonanol (CAS 143-08-8), Linalool (CAS 78-70-6), α-Terpiniol (CAS 98-55-5), Caryophyllne (CAS 87-44-5), n-Hexadecanoic acid (CAS 57-10-3), Geranil acetate (CAS 105-87-3), 7,9-Di-tert-butyl-1-oxaspiro[4.5]deca-6,9-diene-2,8-dione(CAS 82304-66-3), Caprolactama (CAS 105-60-2), 1-Octadecanol (CAS 112-92-5) were used. All reagents were supplied by Sigma-Aldrich Química S.A., (Madrid, Spain) with a purity of >99%.

2.2. Preparation of Films by the Extrusion Technique

Figure 1 schematically illustrates the experimental workflow of the study. The components of each formulation (Table 1) were manually mixed prior to extrusion. Film processing was carried out using a Thermo Scientific Process 11 Parallel Twin-Screw Extruder, equipped with a 40 L/D barrel, 11 mm screw diameter, and a standard push-screw configuration. The extrusion process was performed at temperatures ranging from 80 to 110 °C, from the feeding to the die zone, with a screw rotation speed of 35 rpm. Subsequently, the pellets were compression-molded into films using a hydraulic press (Til Marcon, Sao Paulo, Brazil) at 100 °C for 1 min under a pressure of 0.5 tons.

Table 1. Formulation of films produced by extrusion. All component proportions are expressed as mass percentages (% m/m).

Formulation (%)	Limonene 0%	Limonene 25%	Limonene 50%
Gelatin	50	50	50
Xanthan Gum	5	5	5
Cellulose	10	10	10
Glycerol	35	26.25	17.50
Limonene	0	8.75	17.50

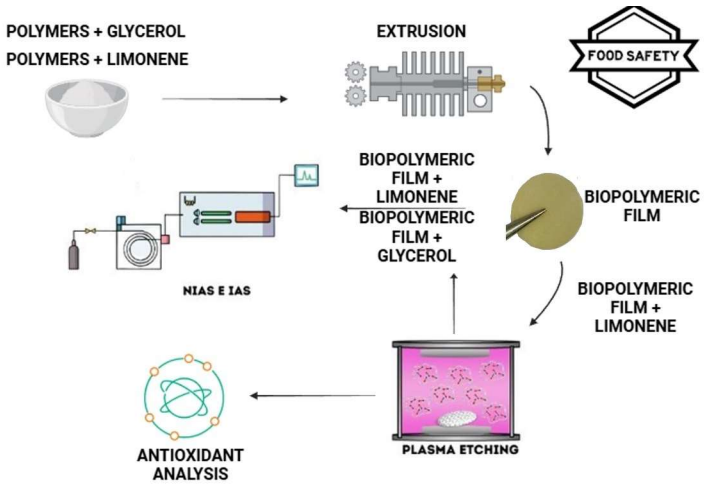

Figure 1. Schematic representation of the present study.

Plasma Treatment

To examine how plasma activation affects the surface characteristics, the films were separated into two experimental sets: one untreated and the other exposed to oxygen plasma. Surface modification was carried out in a capacitively coupled radio-frequency reactor operating at 13.56 MHz. Oxygen served as the process gas and was introduced at a steady rate of 50 sccm using a mass flow controller. The chamber pressure was continuously monitored with an absolute capacitance manometer (MKS Baratron 624B01T, Sao Paulo, Brazil). During treatment, the RF power was fixed at 70 W, and the operating pressure was maintained at 0.70 Torr for a 5 min exposure. After plasma treatment, the chamber was kept under vacuum for an additional 15 min to allow stabilization of the activated surface and to minimize immediate interaction with atmospheric gases. The chamber was then vented to atmospheric pressure, and the samples were removed for subsequent characterization. The samples were categorized based on limonene content and plasma treatment. For clarity, the sample nomenclature, limonene content (% m/m), and plasma treatment are summarized in Table 2.

Table 2. Sample nomenclature of the produced films.

Sample Nomenclature	Limonene Content (%)	Plasma Treatment
Limonene 0%	0	No
Limonene 25%	25	No
Limonene 50%	50	No
Limonene 0%— Plasma	0	Yes
Limonene 25%—Plasma	25	Yes
Limonene 50%—Plasma	50	Yes

2.3. Migration Assay

As described in the European Commission (EU) 10/2011 [25], the migration assay is made in contact between the surface of the material employing food simulators. In this way, the samples were in contact with four types of food simulants: simulant B (ethanol 10%, food and drinks with alcoholic grade), C simulant (acetic acid 3%, slightly acidic foods) and simulant E (tenax, dry foods) for 10 days at 60 °C and D simulant (ethanol 95% and isooctane, fatty foods) for 10 days at 60 °C and 2 days at 20 °C, respectively.

2.4. Instrumental Methods

2.4.1. Gas Chromatography–Mass Spectrometry

The migration analysis was performed using gas chromatography–mass spectrometry (GC-MS) with direct injection, which was used for the ethanol 95% and isooctane simulants, as well as for tenax extracts obtained after two consecutive extractions with ethanol for 1 h in an ultrasonic bath [26]. The equipment used consisted of a gas chromatograph combined with a mass spectrometer detector, both from Agilent Technologies (Madrid, Spain). Compound separation was achieved on an HP-5MS capillary column (30 m × 0.25 µm × 250 µm) from Agilent Technologies (Madrid, Spain). The injection was performed in splitless mode at 250 °C, using helium as the carrier gas with a constant flow rate of 1.0 mL/min. The GC oven was programmed to start at 50 °C (held for 5 min), then increase by 10 °C per minute to 300 °C, and hold at 300 °C for an additional 5 min. Data collection was conducted in SCAN mode over a mass range of 50–450 m/z. For GC–MS analyses, compound identification was based on comparison of mass spectra with commercial spectral libraries (NIST), considering a minimum match factor of 80%, together with retention time consistency and, when available, comparison with analytical standards.

2.4.2. Ultra-High-Pressure Liquid Chromatography–Quadrupole Time-of-Flight Mass Spectrometry (UPLC-QTOF-MS)

Chromatographic analysis was performed using an Acquity™ UHPLC system (Waters, Milford, MA, USA) equipped with a BEH C18 column (2.1 mm × 100 mm, 1.7 µm particle size). The mobile phase was delivered at a constant flow rate of 0.3 mL/min, and the column temperature was set to 35 °C. A gradient elution program was employed, increasing methanol concentration with a 0.1% of acid formic from 5% to 95% over a 13 min run. Tenax extracts obtained after two consecutive extractions with ethanol for 1 h in an ultrasonic bath were directly injected. In contrast, the isooctane extracts were evaporated to dryness and re-dissolved in ethanol. Injection volume was 10 µL. Mass spectrometric detection was carried out using a Xevo G2 QTOF instrument (Waters, Milford, MA, USA) featuring an electrospray ionization (ESI) source operated under atmospheric pressure. The system comprised a hexapole, a quadrupole, a collision cell, and a time-of-flight analyzer. Data was acquired in both positive (ESI^+) ion mode. Corona voltages were set at 2.5 kV for ESI^+. The sampling cone voltage was 30 V. Nitrogen gas was used for desolvation at a flow rate of 500 L/h, with the desolvation temperature maintained at 400 °C. Cone gas flow was set to 20 L/h. Data acquisition was conducted in MSE mode, with a collision energy ramp from 5 to 30 V. The mass range covered was 10 to 1200 Da, with data collected in centroid mode using the sensitivity setting. To maintain mass accuracy and reproducibility, a LockSpray system was employed using leucine-enkephalin (2 ng/mL in water–acetonitrile with 0.1% formic acid) as the lock mass, infused at a rate of 5 µL/min. MassLynx software version 4.1 (Waters, Milford, MA, USA) was used for data processing. For UPLC-QTOF-MS analyses, tentative identification was carried out based on accurate mass measurements, isotopic pattern evaluation, and MS^E fragmentation data, with mass errors below 5 ppm.

2.5. Antioxidant Activity of the Films Produced with Limonene

The antioxidant potential of the films produced with limonene was analyzed using specific equipment, which was developed by Pezo et al. [27] and the system was reported in our previous work Barbosa et al. [28]. Samples were applied to bags of polyethylene (PE), and each sample was placed inside bags with internal dimensions of 150 × 150 mm and heat sealed with an impulse sealer PFS-200 Zhejiang Dongfeng Packing Machine Co. Bags with the samples were placed in a rack and connected to the radical generator system OH•. Vials containing an aqueous solution of sodium salicylate at 2 µg/g were

used to collect the gases from the flow. Samples with possible antioxidant capacity were compared with empty bags and the antioxidant tests were carried out for 24 h. After tests, post-test solutions were analyzed by HPLC with fluorescence detection to monitor the compound 2,5-Dihydroxybenzoic acid, which indicated the antioxidant potential of the composite materials.

2.6. Statistical Analysis

All experiments were performed with real replicates ($n \geq 3$), and results are expressed as mean ± standard deviation. Statistical analysis was carried out using one-way analysis of variance (ANOVA), followed by Tukey's post hoc test to evaluate significant differences between samples. Differences were considered statistically significant at $p < 0.05$. Statistical analyses were performed using OriginPro (v 9.7, OriginLab Corporation, Northampton, MA, USA).

3. Results and Discussion

The results are presented and discussed below with a focus on migration behavior, plasticizer type, oxygen plasma treatment, and the influence of food simulant characteristics.

3.1. Migration Assays

Films were immersed in each simulant and incubated at 60 °C for 10 days for the simulants ethanol 10%, acetic acid 3%, and ethanol 95%. During this period, the films in the ethanol 10% and acetic acid 3% simulants exhibited visual degradation due to their high hydrophilicity, as shown in Figure 2, making these simulants unsuitable for further analysis. Ethanol 95% was nevertheless maintained as a food simulant in this study, despite inducing partial swelling of the films, because it is defined in Regulation (EU) No. 10/2011 as a fatty food simulant and is commonly used to represent a highly conservative worst-case scenario for migration assessment. Although such conditions do not reflect typical real food contact, they allow the overestimation of migration phenomena and facilitate the detection and identification of potential IAS and NIAS. Therefore, an additional migration test was performed using tenax as a solid food simulant to obtain further results and achieve a deeper understanding of the material's performance as a potential food packaging.

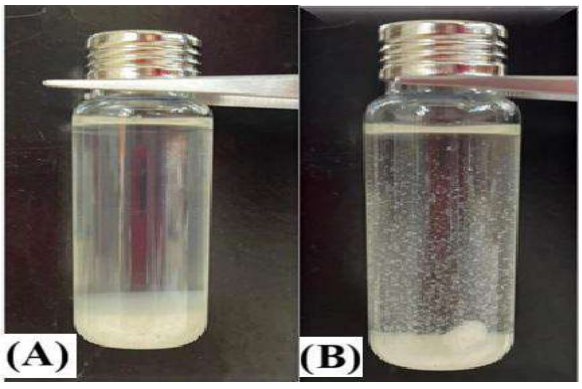

Figure 2. Films after 10 days of contact with ethanol 10% (**A**) and acetic acid 3% (**B**), showing matrix dissolution.

3.2. Volatile Compounds Migration

Table 3 summarizes the volatile compounds migrated into ethanol 95% and the SM 1 are the analytical parameters for GC-MS, highlighting the influence of limonene content and oxygen plasma treatment on terpene release. Accordingly, compounds were classified as either confidently identified or tentatively identified NIAS, depending on the level of an-

alytical evidence available. Ethanol 95% was retained in the study as it is recommended by Regulation (EU) No. 10/2011 as a severe food simulant for fatty foods and is widely used to represent worst-case migration conditions, despite its known swelling effect on hydrophilic polymer matrices. The incorporation of limonene demonstrated a significant alteration in the release profile of volatile and semi-volatile compounds. In control films (limonene 0%), migration was mainly restricted to polar substances such as glycerol (22.6 ± 3.3 mg/kg) and 1,2,3-propane-triol acetate (11.1 ± 0.9 mg/kg). However, the addition of limonene promoted the migration of a wide range of terpenes, including limonene itself, β-pinene, γ -terpinene, and geraniol. Migration showed a proportional increase with limonene content, with limonene rising from 475 ± 26 mg/kg (Limonene 25%) to 808 ± 56 mg/kg (Limonene 50%). According to Nakonechnyi et al. [29], the release or migration rate of limonene strongly depends on the nature and composition of the polymer matrix, since factors such as the structure, polarity, crystallinity, and presence of microcracks of the material influence the diffusion process and the output of the compound. In addition, migration behavior is also governed by the physicochemical properties of the permeant itself. In the case of limonene, its low molecular weight, hydrophobic character, and high affinity for non-polar simulants favor its diffusion and partitioning into fatty media [30]. Similarly, Nasha et al. [30] used polysaccharide matrices (CMC, pectin, and starch) to evaluate the influence of the retention and stability of limonene and highlighted that the migration of limonene in polysaccharide films strongly depends on the viscosity and structural integrity of the matrix.

Table 3. Quantification of volatile migrant compounds in ethanol 95% simulant.

TR	Compound	Quantification Standard	Migration Values mg/kg of Ethanol 95%					
			Limonene 0%	Limonene 25%	Limonene 50%	Limonene 0%—Plasma	Limonene 25%—Plasma	Limonene 50%—Plasma
8.93	β-Pinene	β-Pinene	—	386 ± 28.1	534 ± 28.5	—	525 ± 48.5	724 ± 1.74
7.97	α-Pinene *	β-Pinene	—	142 ± 34.3	243 ± 40.5	—	145 ± 38.4	241 ± 41.2
12.91	Glycerol	Glycerol	22.6 ± 3.28	14.4 ± 0.85	10.6 ± 0.22	17.7 ± 1.43	13.6 ± 1.35	13.8 ± 1.01
11.23	1,2,3-Propanetriol,1-acetate *	Glycerol	11.1 ± 0.9	4.64 ± 0.47	6.29 ± 3.53	13.8 ± 0.42	6.06 ± 0.28	3.59 ± 0.09
10.07	Limonene	Limonene	—	475 ± 26.3	808 ± 56.4	—	612 ± 49.3	827 ± 83.3
12.02	Limonene oxide, cis *	Limonene	—	0.06 ± 0.02	0.09 ± 0.02	—	0.07 ± 0.01	0.07 ± 0.01
13.88	Geraniol	Geraniol	—	8.67 ± 1.35	31.3 ± 0.23	—	12.3 ± 2.32	22.2 ± 1.65
10.70	γ-Terpinene	γ-Terpinene	—	76.7 ± 6.6	269 ± 20.3	—	92.8 ± 8.03	277 ± 1.42
13.68	Citronelol	Citronelol	—	42.0 ± 14.3	99.6 ± 44.9	—	42.3 ± 14.1	119 ± 18.3
12.18	1-Nonanol	1-Nonanol	—	1.88 ± 0.57	12.8 ± 0.13	—	1.82 ± 0.37	7.97 ± 0.49
11.41	Linalool	Linalool	—	7.24 ± 1.11	19.6 ± 0.32	—	9.59 ± 2.33	19.0 ± 1.52
9.30	β-Myrcene *	Linalool	—	17.0 ± 4.52	94.3 ± 5.96	—	27.7 ± 4.03	95.7 ± 1.94
12.83	α-Terpiniol	A-Terpiniol	—	72.6 ± 10.1	50.5 ± 13.7	—	83.2 ± 18.1	80.0 ± 12.53
17.38	β-Bisabolene *	α-Terpiniol	—	76.3 ± 4.32	124 ± 6.14	—	102 ± 8.24	115 ± 64.13
16.33	Caryophyllne	Caryophyllne	—	25.1 ± 1.63	40.5 ± 6.54	—	29.8 ± 3.71	34.3 ± 2.92
22.40	n-Hexadecanoic ac.	n-Hexadecanoic ac.	—	0.50 ± 1.20	15.2 ± 5.43	—	0.84 ± 0.36	11.2 ± 1.24
15.90	Geranil Acetate	Geranil Acetate	—	0.76 ± 0.06	2.16 ± 0.41	—	1.17 ± 0.09	1.23 ± 1.69
15.65	2,6-Octadien-1-ol, 3,7-dimethyl-, (Z) *	Geranil Acetate	—	7.57 ± 0.67	14.0 ± 0.54	—	10.9 ± 1.14	13.3 ± 0.95
21.92	7,9 Di-tert. Butyl	7,9 Di-tert. Butyl-	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
20.19	Glycyl-L-proline *	Caprolactama	2.19 ± 0.16	2.38 ± 0.15	3.28 ± 0.18	2.69 ± 0.13	3.41 ± 0.12	3.03 ± 0.18
14.30	1-Decanol *	1-Octadecanol	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
12.98	Terpinen-4-ol *	γ-Terpinene	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

* NIAS without available reference standards were considered tentatively identified with a match > 80%.

Plasma treatment was associated with higher terpene migration, with maximum values for limonene and for β-pinene in films containing 50% limonene. Although molecular size can influence diffusion, the observed migration behavior cannot be explained solely by molecular weight differences between terpenes and glycerol. Instead, polarity and molecu-

lar affinity with the polymer matrix play a dominant role. Terpenes such as limonene and β-pinene are non-polar, low-molecular-weight compounds with a high affinity for fatty simulants, which favors their partitioning and diffusion compared to more polar molecules such as glycerol. Similar behavior has been reported for polysaccharide-based films, in which the migration and retention of hydrophobic compounds strongly depend on matrix permeant affinity and structural organization [29,30]. Moreover, plasma treatment may have contributed to an increase terpene migration by modifying the surface morphology of the films. Plasma-induced etching is known to increase surface roughness and effective surface area, promoting molecular mobility and facilitating diffusion pathways [17,18]. In addition, plasma treatment can weaken intermolecular interactions within polymer networks and induce surface activation, which could further favor the release of volatile compounds such as terpenes [16,21].

In contrast, the migration of glycerol decreased in the presence of limonene, and plasma resulted in comparable migration levels. This behavior can be attributed to the higher polarity of glycerol and its strong hydrogen-bonding interactions with the polymer matrix, which limits its molecular mobility even after plasma exposure [10,11]. Additionally, competitive interactions between glycerol and limonene within the matrix may further restrict glycerol diffusion, reinforcing the central role of polarity and molecular affinity in governing migration behavior. These results are consistent with the expectation that differences in plasticizer polarity and matrix affinity govern migration behavior in biopolymer-based films.

Several compounds, including n-hexadecanoic acid, 1-nonanol and geranyl acetate, were detected only in samples containing limonene, probably due to ester hydrolysis or oxidative degradation reactions induced by processing [29,30]. Despite their natural origin and the GRAS (Generally Recognized as Safe) status attributed to many terpenes, the migration levels measured largely exceeded the overall migration limit of 60 mg/kg established by EU Regulation No. 10/2011 [31]. However, this regulation was originally designed for conventional plastic materials and has not been specifically adapted to natural or bio-based polymers. This regulatory challenge highlights the need for careful interpretation of migration data, particularly under worst-case testing conditions [32]. Consequently, certain naturally occurring substances, such as terpenes, may exceed the established limits, even though they are commonly found in foods and ingested at much higher levels without posing toxicological risk [31]. These elevated migration values observed in this study indicate strong solvent matrix interactions, leading to partial polymer chain dissolution and extraction of low molar mass constituents. Lopéz Sanvicente et al. [32] worked with commercial food contact material (FCM) considered bio-based and/or biodegradable to tentatively identify potential migrants to food. As a result, they obtained more than 200 compounds, of which only 29 were identified compounds included in Regulation (EU) 10/2011. This finding highlights the need for improved guidance regarding the interpretation of migration data obtained under severe testing conditions.

Overall, limonene promoted the release of hydrophobic volatiles, while plasma treatment was associated with an increased diffusion of terpenes. These findings reveal complex interdependencies between film composition and surface modification, emphasizing the importance of aligning safety assessment frameworks with the specific nature of bio-based active packaging systems.

Isooctane migration results (Table 4 and Table S2) revealed a clear dependence between limonene content and its migration into the simulant. Migration ranged from 0.61 mg/kg at limonene 25% to 1.82 mg/kg at limonene 50%, while plasma-treated samples exhibited lower limonene release, with values of 1.16 mg/kg. Oxidation derivatives of limonene, including γ-terpinene, α-terpineol and β-pinene, were detected in the formulations con-

taining limonene, showing higher concentrations at increased limonene contents [12,13,15]. These results confirm that the films allow the migration of lipophilic compounds as well as volatile NIAS generated through oxidation or isomerization reactions of limonene [14,30].

Table 4. Quantification of volatile migrant compounds to isooctane simulant.

TR	Compound	Quantification Standard	Migration Values mg/kg of Isooctane					
			Limonene 0%	Limonene 25%	Limonene 50%	Limonene 0%—Plasma	Limonene 25%—Plasma	Limonene 50%—Plasma
10.70	γ-Terpinene	γ-Terpinene	—	0.11 ± 0.01	0.41 ± 0.24	—	0.22 ± 0.04	0.43 ± 0.02
12.83	α-Terpiniol	α-Terpiniol	—	0.32 ± 0.09	0.45 ± 0.18	—	0.33 ± 0.08	0.46 ± 0.04
10.07	Limonene	Limonene	—	0.61 ± 0.09	1.82 ± 0.82	—	0.40 ± 0.04	1.16 ± 0.12
8.93	β-Pinene	β-Pinene	—	0.86 ± 0.09	0.98 ± 0.08	—	0.84 ± 0.05	0.91 ± 0.05
13.68	Citronelol	Citronelol	—	<LOQ	<LOQ	—	<LOQ	<LOQ
15.90	Geranil Acetate	Geranil Acetate	—	<LOQ	<LOQ	—	<LOQ	<LOQ
13.88	Geraniol	Geraniol	—	<LOQ	<LOQ	—	<LOQ	<LOQ

Other volatile compounds, such as citronellol, geraniol, and geranyl acetate, were below the LOQ, suggesting that their formation pathways are not favored under these conditions [29]. Overall, although total migration levels are low, limonene degradation processes generate NIAS that should be considered in the safety assessment of these bio-based films for contact with fatty foods.

A clear difference in migration behavior was observed depending on the fatty food simulant used (ethanol 95% or isooctane), which is normal according to the literature [31,33]. The markedly higher migration observed in ethanol 95% should therefore be interpreted as a conservative upper-bound scenario, as the strong solvent character of ethanol promotes polymer swelling and can overestimate the release of low-molecular-weight compounds compared to real fatty foods. Ethanol 95% promoted extensive migration of terpenes, with values for limonene, β-pinene, and γ-terpinene, which exceeded the overall migration limit of 60 mg/kg established by Regulation (EU) No. 10/2011 [31]. In this context, its use in the present study aimed to provide conservative estimates of migration behavior, rather than to represent realistic food contact conditions. As such, migration values obtained with this simulant tend to overestimate the release of low-molecular-weight compounds compared to real food systems. In contrast, migration into tenax and isooctane, which better represent dry and fatty food contact conditions, remained well below the overall migration limit. This indicates that the observed exceedance in ethanol 95% does not necessarily preclude the use of these materials for specific food packaging applications, particularly for dry or low-fat foods. These results reflect the distinct extraction capacities of the simulants [33]. Ethanol, owing to its amphiphilic character, can swell the polymer matrix and solubilize both polar and non-polar compounds, thereby leading to an overestimation of the potential migration of terpenes. On the other hand, isooctane, a non-polar hydrocarbon, showed limited interaction with the hydrophilic polymer network, resulting in low release [31,33,34]. Plasma treatment was associated with higher migration levels in ethanol, particularly for terpenes, but presented only minor effects in isooctane. This suggests that surface modifications are more relevant under polar conditions, where polymer solvent interactions are stronger.

From a regulatory perspective, the comparison of the measured migration levels with the overall migration limit (OML) when ethanol 95% was used as food simulant should be interpreted within the context of a conservative worst-case assessment. Ethanol 95% strongly interacts with hydrophilic biopolymer matrices, promoting swelling and extraction of low-molecular-weight compounds, and therefore tends to overestimate migration relative to real food systems. In contrast, migration results obtained with isooctane and

tenax, which are considered more representative of fatty and dry food contact, respectively, were well below the OML, indicating a substantially lower migration potential under more realistic conditions. Accordingly, the OML exceedance observed under worst-case conditions does not necessarily preclude the use of these materials but rather indicates that their potential applications should be carefully defined, favoring dry or low-fat foods and requiring case-specific assessment for contact with fatty foods.

Table 5 summarizes the volatile compounds migrated into tenax, providing insight into the behavior of NIAS and IAS under dry-food simulant conditions. Migration tests revealed the presence of both IAS and NIAS in all formulations (Tables 5 and S3). Glycerol was the main intentionally added plasticizer detected, and its migration was not noticeably influenced by the partial substitution with limonene. Limonene was released in low concentrations from films containing limonene, confirming its limited stability and release under the applied conditions.

Table 5. Quantification table of volatile migrant compounds to tenax simulant.

TR	Compound	Quantification Standard	Migration Values mg/kg of Tenax					
			Limonene 0%	Limonene 25%	Limonene 50%	Limonene 0%—Plasma	Limonene 25%—Plasma	Limonene 50%—Plasma
12.91	Glycerol	Glycerol	2.68 ± 0.67	2.62 ± 0.87	2.15 ± 0.96	2.20 ± 0.69	2.52 ± 0.28	2.51 ± 0.43
11.23	1,2,3-Propanetriol, 1-acetate *	Glycerol	1.11 ± 0.59	0.56 ± 0.06	2.61 ± 0.87	1.94 ± 0.13	0.52 ± 0.09	0.22 ± 0.04
10.07	Limonene	Limonene	—	0.17 ± 0.03	0.27 ± 0.04	—	0.06 ± 0.06	0.11 ± 0.08
13.88	Geraniol	Geraniol	—	0.15 ± 0.01	0.19 ± 0.09	—	0.08 ± 0.17	0.13 ± 0.03
13.68	Citronelol	Citronelol	—	0.12 ± 0.05	0.11 ± 0.06	—	0.10 ± 0.09	0.09 ± 0.02
12.83	α-Terpiniol	α-Terpiniol	—	0.02 ± 0.01	0.02 ± 0.01	—	0.01 ± 0.01	0.01 ± 0.01
21.92	7,9 Di-tert. Butyl	7,9 Di-tert. Butyl	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
12.02	Limonene oxide, cis *	Limonene	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
10.70	γ-Terpinene	γ-Terpinene	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
12.75	Terpinen-4-ol *	γ-Terpinene	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

* NIAS without available reference standards were considered tentatively identified with a match > 80%.

Several derivatives were also identified, as shown in Table S3. The detection of 1,2,3-propanetriol, 1-acetate in all samples, particularly in the limonene 50% formulation, suggests chemical modification of glycerol during processing, probably due to acetylation or dehydration reactions. Moreover, the appearance of geraniol, citronellol, and α-terpineol exclusively in limonene containing films indicates oxidative or isomerization pathways of limonene, as observed before, in agreement with the literature on terpene degradation [29,30]. Although their concentrations were low, their presence confirms that limonene can generate NIAS when incorporated into biopolymer matrices.

Plasma-treated films exhibited migration profiles comparable to the untreated ones, with slightly lower concentrations of limonene and its derivatives. Although these differences are small, they may indicate partial plasma-induced oxidation or surface modification, which could promote either volatilization or immobilization of limonene and its oxidation products within the polymer matrix [13,14]. In contrast, glycerol migration remained largely unaffected by plasma treatment, likely due to its strong affinity for the polymer network and its intrinsic mobility in dry simulants such as tenax. Overall, these results suggest that while glycerol migration is relatively stable and predictable, the incorporation of limonene introduces minor but detectable chemical transformations, generating additional NIAS through oxidation or rearrangement pathways. Even though their migration levels are low, the formation of these compounds highlights the chemical sensitivity of terpene-based additives during processing and post-treatment steps. Therefore, migration results obtained with tenax and isooctane are more representative of practical food contact scenarios

and were considered particularly relevant for evaluating the potential applicability of the developed films.

3.3. Non-Volatile Compounds

No migration of non-volatile IAS or NIAS was detected in the samples analyzed under the applied experimental conditions. When ethanol 95% was used as a food simulant, the extensive release of volatile compounds largely exceeded regulatory limits, and therefore the analysis of non-volatile compounds in this simulant was not further pursued, as the material behavior was dominated by solvent-induced swelling effects. For isooctane (shown in the Figure 3) and tenax simulants, UPLC-QTOF-MS analysis did not reveal the presence of non-volatile migrants when compared with the corresponding blank chromatograms. Under the applied analytical conditions, the method exhibited sufficient sensitivity for the detection of non-volatile compounds typically reported in food contact material studies; however, no additional signals attributable to the analyzed materials were observed.

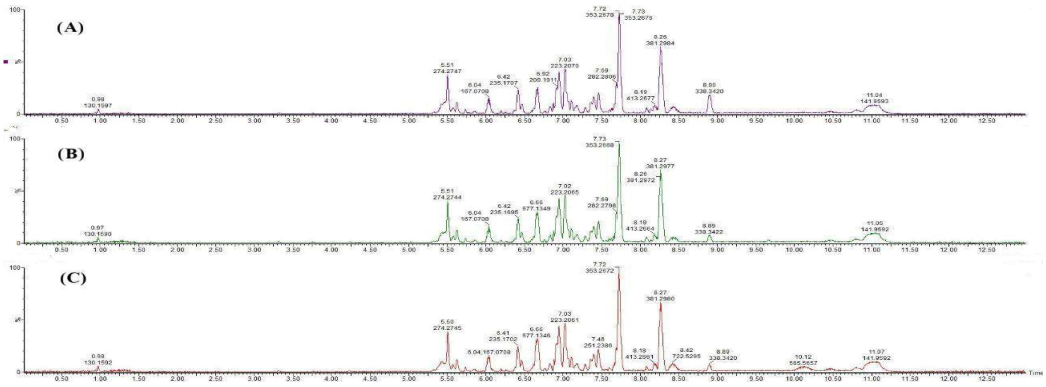

Figure 3. Chromatograms after migration to iso-octane for the samples, where the top trace corresponds to the control (isooctane alone) (**A**), the middle to limonene 50% (**B**), and the bottom to limonene 50%—plasma (**C**).

This behavior can be explained by several complementary factors, including the marked difference in polarity between potential migrants, such as polar oligomers derived from gelatin, cellulose, or glycerol, and the predominantly non-polar nature of isooctane, which makes migration thermodynamically unfavorable, as previously reported for PLA oligomers in liquid simulants [31,33,35]. In addition, strong intermolecular interactions within the hydrophilic biopolymer matrix restrict molecular mobility and limit the diffusion of larger or more polar NIAS [36]. Finally, although tenax is an efficient sorbent for volatile compounds, its capacity to retain non-volatile substances that do not readily vaporize is limited [37–40].

Overall, these findings indicate that the tested biopolymer formulations are unlikely to release detectable IAS or NIAS under the conditions studied, supporting their potential suitability as safe materials for food packaging applications.

3.4. Antioxidant Assay

The antioxidant activity assay, Table 6, demonstrated that the incorporation of limonene conferred significant antioxidant capacity to the films. Films with 25% and 50% limonene reached antioxidant activities of 51.78% and 77.38%, respectively, confirming a statistically significant dose-dependent effect of the bioactive compound ($p < 0.05$). This result is consistent with the well-documented antioxidant properties of monoterpenes, particularly limonene, which can neutralize hydroxyl radicals and delay oxidative processes. According to Viana et al. [41], the antioxidant activity of limonene arises primarily from its

ability to donate hydrogen atoms. The allylic hydrogens present in limonene are readily abstracted by free radicals, leading to radical stabilization and subsequent termination of oxidative chain reaction.

Table 6. Antioxidant capacity in percentage of the samples.

Formulation	Antioxidant Capacity (%)
Limonene 0%	0 [a]
Limonene 25%	51.78 ± 5.82 [a]
Limonene 50%	77.38 ± 7.53 [c]
Limonene 0%—Plasma	0 [a]
Limonene 25%—Plasma	65.87 ± 8.24 [c]
Limonene 50%—Plasma	83.86 ± 6.36 [d]

Different superscript letters within the same column indicate statistically significant differences ($p < 0.05$).

Plasma treatment resulted in a statistically significant enhancement of the antioxidant activity of films containing limonene ($p < 0.05$), increasing the antioxidant capacity to 65.87% and 83.86% for the 25% and 50% limonene formulations, respectively. In contrast, plasma treatment did not induce antioxidant activity in films without limonene, indicating that the observed effect is associated with the presence of the bioactive compound. The enhancement observed after plasma treatment may be attributed to a synergistic effect between the intrinsic antioxidant properties of limonene and plasma-induced surface modifications. Plasma exposure can promote the formation of additional hydrophilic functional groups, such as hydroxyl and carbonyl groups, which may contribute to the scavenging of reactive radical species.

A comparable effect was reported by Basak and Annapure [42] for apple pectin modified by cold atmospheric-pressure plasma, where antioxidant capacity increased with plasma exposure time. The authors associated this behavior with the incorporation of oxygen-containing functional groups generated by reactive oxygen and nitrogen species (ROS and RNS) during plasma treatment. In plasma systems, ROS and RNS are primarily generated from the ionized working gas; however, their formation can also be promoted upon exposure of activated surfaces to ambient air. In the present study, such surface reactions may have occurred within the gelatin/xanthan gum/cellulose matrix, contributing to the observed enhancement in antioxidant performance. Taken together, the results of the migration assays, NIAS screening, and antioxidant evaluation provide an integrated view of the performance safety balance of plasma-treated biopolymer films. By combining surface modification, formulation effects, and the use of different food simulants, this study highlights how processing and testing conditions jointly influence migration behavior and functional properties, rather than focusing on a single isolated parameter.

4. Conclusions

The migration behavior of plasticizers and their derivatives from the films studied were shown to be strongly influenced by both the polarity of the food simulant and the chemical nature of the plasticizer under the experimental conditions evaluated. The incompatibility of the formulations with aqueous simulants was evidenced by the perceptible dissolution of the polymer matrix, indicating a pronounced sensitivity of these biopolymeric systems to highly hydrophilic environments. Glycerol predominantly migrated into hydrophilic media, whereas limonene and its volatile derivatives exhibited higher migration levels in fatty simulants, highlighting the central role of molecular polarity and matrix simulant affinity in governing migration behavior. Surface modification by oxygen plasma resulted in modest changes in migration profiles, particularly for volatile terpenes, depending on the simulant employed.

Although overall migration levels were low under most of the tested conditions, the formation of non-intentionally added substances (NIAS), especially those arising from limonene degradation or transformation, underscores the importance of considering additive chemical stability and processing effects when assessing the safety of bio-based films for food contact applications. These findings are particularly relevant given that migration phenomena and NIAS generation in biopolymeric packaging materials remain comparatively underexplored.

In parallel, the incorporation of limonene conferred antioxidant functionality to the films, and this effect was further enhanced by plasma treatment in formulations containing the bioactive compound, providing an additional functional benefit beyond migration behavior. The comparison of the measured migration levels with the regulatory overall migration limit threshold under worst-case conditions emphasizes the importance of defining appropriate food contact applications, rather than indicating a general unsuitability of the material.

Overall, the results indicate that film composition, surface modification, and simulant characteristics jointly influence migration behavior and functional performance. This highlights the need for comprehensive, case-specific assessments in the development of biopolymer-based food packaging materials. In this context, the present study also points to limitations of current regulatory frameworks, originally developed for conventional plastics, in fully capturing the specific behavior of biopolymeric and bioactive packaging systems.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/foods15050867/s1, Table S1. Table of analytical parameters for the quantification of volatile compounds in ethanol 95% food simulant. Table S2. Table of analytical parameters for the quantification of volatile compounds in isooctane food simulant. Table S3. Table of analytical parameters for the quantification of volatile compounds in ethanol.

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References

1. Tran, T.T.V.; Nguyen, N.N.; Nguyen, Q.C.; Nguyen, T.P.; Lien, T.N. Gelatin/carboxymethyl cellulose edible films: Modification of physical properties by different hydrocolloids and application in beef preservation in combination with shallot waste powder. *RSC Adv.* **2023**, *13*, 9998–10004. [CrossRef]
2. Park, S.; Oh, Y.; Yun, J.; Yoo, E.; Jung, D.; Park, K.S.; Oh, K.K.; Lee, S.H. Characterization of blended cellulose/biopolymer films prepared using ionic liquid. *Cellulose* **2020**, *27*, 5101–5119. [CrossRef]
3. Pereira, J.F.; Lonni, A.A.S.G.; Mali, S. Development of biopolymeric films with addition of vitamin C and catuaba extract as natural antioxidants. *Prep. Biochem. Biotechnol.* **2021**, *52*, 1–10. [CrossRef] [PubMed]

4. Leite, L.S.F.; Bilatto, S.; Paschoalin, R.T.; Soares, A.C.; Moreira, F.K.V.; Oliveira, O.N.; Mattoso, L.H.C.; Bras, J. Eco-friendly gelatin films with rosin-grafted cellulose nanocrystals for antimicrobial packaging. *Int. J. Biol. Macromol.* **2020**, *165*, 2974–2983. [CrossRef] [PubMed]
5. Pereira, J.F.; Marim, B.M.; Simões, B.M.; Yamashita, F.; Mali, S. Hydrogels based on gelatin, xanthan gum, and cellulose obtained by reactive extrusion and thermopressing processes. *Prep. Biochem. Biotechnol.* **2023**, *1*, 942–953. [CrossRef]
6. Rukmanikrishnan, B.; Ismail, F.R.M.; Manoharan, R.K.; Kim, S.S.; Lee, J. Blends of gellan gum/xanthan gum/zinc oxide-based nanocomposites for packaging application: Rheological and antimicrobial properties. *Int. J. Biol. Macromol.* **2020**, *148*, 1182–1189. [CrossRef]
7. Chen, J.; Zheng, M.; Tan, K.B.; Lin, J.; Chen, M.; Zhu, Y. Polyvinyl alcohol/xanthan gum composite film with excellent food packaging, storage and biodegradation capability as potential environmentally-friendly alternative to commercial plastic bag. *Int. J. Biol. Macromol.* **2022**, *212*, 402–411. [CrossRef]
8. Ribeiro, A.C.R.; Rodrigues, M.B.B.; Ribes, D.D.; Cholant, C.M.; Lima, G.S.; Valim, G.C.; Delucis, R.A.; Oliveira, A.D.; Carreño, N.L.V.; Gatto, D.A.; et al. Effect of xanthan gum on the physical and chemical features of microfibrillated cellulose films plasticized by glycerol. *Biomass Convers. Biorefin* **2023**, *14*, 22203–22214. [CrossRef]
9. Montoille, L.; Vicencio, C.M.; Fontalba, D.; Ortiz, J.A.; Moreno-Serna, V.; Peponi, L.; Matiacevich, S.; Zapata, S.A. Study of the effect of the addition of plasticizers on the physical properties of biodegradable films based on kefiran for potential application as food packaging. *Food Chem.* **2021**, *360*, 129966. [CrossRef]
10. Ben, Z.Y.; Samsudin, H.; Yhaya, M.F. Glycerol: Its properties, polymer synthesis, and applications in starch-based films. *Eur. Polym. J.* **2022**, *175*, 111377. [CrossRef]
11. Tarique, J.; Sapuan, S.M.; Khalina, A. Effect of glycerol plasticizer loading on the physical, mechanical, thermal, and barrier properties of arrowroot (*Maranta arundinacea*) starch biopolymers. *Sci. Rep.* **2021**, *11*, 13900. [CrossRef]
12. Gomez-Caturla, J.; Tejada-Oliveros, R.; Ivorra-Martinez, J.; Garcia-Sanoguera, D.; Balart, R.; Garcia-Garcia, D. Development and Characterization of New Environmentally Friendly Polylactide Formulations with Terpenoid-Based Plasticizers with Improved Ductility. *J. Polym. Environ.* **2024**, *32*, 749–762. [CrossRef]
13. Schutz, G.F.; Alves, R.M.V.; Delarmelina, C.; Duarte, M.C.T.; Vieira, R.P. Limonene and its derived oligomer as bioactive additives in starch/coffee husks biocomposites for food packaging applications. *Int. J. Biol. Macromol.* **2024**, *260*, 129482. [CrossRef]
14. Lan, W.; Wang, S.; Chen, M.; Sameen, D.E.; Lee, K.; Liu, Y. Developing poly(vinyl alcohol)/chitosan films incorporate with d-limonene: Study of structural, antibacterial, and fruit preservation properties. *Int. J. Biol. Macromol.* **2020**, *145*, 722–732. [CrossRef] [PubMed]
15. Fortunati, E.; Luzi, F.; Puglia, D.; Dominici, F.; Santulli, C.; Kenny, J.M.; Torre, L. Investigation of thermo-mechanical, chemical and degradative properties of PLA-limonene films reinforced with cellulose nanocrystals extracted from Phormium tenax leaves. *Eur. Polym. J.* **2014**, *56*, 77–91. [CrossRef]
16. Abd Jelil, R. A review of low-temperature plasma treatment of textile materials. *J. Mater. Sci.* **2015**, *50*, 5913–5943. [CrossRef]
17. Phan, L.T.; Yoon, S.M.; Moon, M.W. Plasma-based nanostructuring of polymers: A review. *Polymers* **2017**, *9*, 417. [CrossRef] [PubMed]
18. Vesel, A.; Mozetic, M. New developments in surface functionalization of polymers using controlled plasma treatments. *J. Phys. D: Appl. Phys.* **2017**, *50*, 293001. [CrossRef]
19. Jesus, L.A.O. Desenvolvimento e Modificação a Plasma de Materiais a Base de Poli (Ácido Lático)/α-Ag_2WO_4 Com Potencial Ação Antimicrobiana. Bachelor's Thesis, Universidade Federal de São Carlos, São Carlos, Brazil, 2022.
20. Wang, F.; Zhao, S.; Zhang, X.; Su, Z. Interfacial solar evaporation based on Janus films: An effective strategy to improve salt tolerance and antifouling performance. *Desalination* **2022**, *543*, 116085. [CrossRef]
21. Hoque, M.; McDonagh, C.; Tiwari, B.K.; Kerry, J.P.; Pathania, S. Effect of Cold Plasma Treatment on the Packaging Properties of Biopolymer-Based Films: A Review. *Appl. Sci.* **2022**, *12*, 1346. [CrossRef]
22. Canellas, E.; Nerín, C.; Moore, R.; Silcock, P. New UPLC coupled to mass spectrometry approaches for screening of non-volatile compounds as potential migrants from adhesives used in food packaging materials. *Anal. Chim. Acta* **2010**, *666*, 62–69. [CrossRef]
23. Wrona, M.; Vera, P.; Pezo, D.; Nerín, C. Identification and quantification of odours from oxobiodegradable polyethylene oxidised under a free radical flow by headspace solid-phase microextraction followed by gas chromatography-olfactometry-mass spectrometry. *Talanta* **2017**, *172*, 37–44. [CrossRef] [PubMed]
24. Kato, L.S.; Conte-Junior, C.A. Safety of plastic food packaging: The challenges about non-intentionally added substances (NIAS) discovery, identification and risk assessment. *Polymers* **2021**, *13*, 2077. [CrossRef] [PubMed]
25. Commission Regulation (EU) No 10/2011 of 14 January 2011 on Plastic Materials and Articles Intended to Come into Contact with Food Text with EEA Relevance. Available online: http://https://www.legislation.gov.uk/eur/2011/10 (accessed on 25 February 2026).
26. Canellas, E.; Vera, P.; Nerín, C. Multiple headspace-solid phase microextraction for the determination of migrants coming from a self-stick label in fresh sausage. *Food Chem.* **2016**, *197*, 24–29. [CrossRef]

27. Pezo, D.; Salafranca, J.; Nerín, C. Determination of the antioxidant capacity of active food packagings by in situ gas-phase hydroxyl radical generation and high-performance liquid chromatography–fluorescence detection. *J. Chromatogr. A* **2008**, *1178*, 126–133. [CrossRef] [PubMed]
28. Barbosa, M.L.; Oliveira, L.M.D.; Paiva, R.; Dametto, A.C.; Dias, D.D.S.; Ribeiro, C.A.; Cruz, S.A. Evaluation the potential of onion/laponite composites films for sustainable food packaging with enhanced UV protection and antioxidant capacity. *Molecules* **2023**, *28*, 6829. [CrossRef]
29. Nakonechnyi, V.; Havryliak, V.; Lubenets, V. Controlled release of D-limonene from biodegradable films with enzymatic treatment. *Polymers* **2025**, *17*, 2238. [CrossRef]
30. Nahas, E.O.; Furtado, G.F.; Lopes, M.S.; Silva, E.K. From Emulsions to Films: The Role of Polysaccharide Matrices in Essential Oil Retention Within Active Packaging Films. *Foods* **2025**, *14*, 1501. [CrossRef]
31. Gupta, R.K.; Pipliya, S.; Karunanithi, S.; Eswaran U, G.M.; Kumar, S.; Mandliya, S.; Srivastav, P.P.; Suthar, T.; Shaikh, A.M.; Harsányi, E.; et al. Migration of Chemical Compounds from Packaging Materials into Packaged Foods: Interaction, Mechanism, Assessment, and Regulations. *Foods* **2024**, *13*, 3125. [CrossRef]
32. López Sanvicente, E.; Barbosa-Pereira, L.; Sendón, R.; Bernaldo de Quirós, A.R.; Lestido-Cardama, A. Identification of Potential Migrants in Food Contact Materials Labeled as Bio-Based and/or Biodegradable by GC-MS. *Coatings* **2025**, *15*, 751. [CrossRef]
33. Spinei, M.; Oroian, M. Identification and quantification of intentionally and non-intentionally added substances occurring from biodegradable food packaging: A review. *Food Res. Int.* **2025**, *218*, 116880. [CrossRef] [PubMed]
34. Guazzotti, V.; Gruner, A.; Juric, M.; Hendrich, V.; Störmer, A.; Welle, F. Migration Testing of GPPS and HIPS Polymers: Swelling Effect Caused by Food Simulants Compared to Real Foods. *Molecules* **2022**, *27*, 823. [CrossRef] [PubMed]
35. Ubeda, S.; Aznar, M.; Alfaro, P.; Nerín, C. Migration of oligomers from a food contact biopolymer based on polylactic acid (PLA) and polyester. *Anal. Bioanal. Chem.* **2019**, *411*, 5951–5963. [CrossRef] [PubMed]
36. Rubio, L.; Valverde-Som, L.; Sarabia, L.A.; Ortiz, M.C. The behaviour of Tenax as food simulant in the migration of polymer additives from food contact materials by means of gas chromatography/mass spectrometry and PARAFAC. *J. Chromatogr. A* **2019**, *1589*, 18–29. [CrossRef]
37. Van Den Houwe, K.; Van de Velde, S.; Evrard, C.; Van Hoeck, E.; Van Loco, J.; Bolle, F. Evaluation of the migration of 15 photo-initiators from cardboard packaging into Tenax® using ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS). *Food Addit. Contam. Part A* **2014**, *31*, 767–775. [CrossRef]
38. Vera, P.; Canellas, E.; Nerín, C. Identification of non-volatile migrant compounds and NIAS in polypropylene films used as food packaging characterized by UPLC-MS/QTOF. *Talanta* **2018**, *188*, 750–762. [CrossRef]
39. Vera, P.; Canellas, E.; Dreolin, N.; Goshawk, J.; Nerín, C. The analysis of the migration of per- and polyfluoroalkyl substances (PFAS) from food contact materials using ultrahigh-performance liquid chromatography coupled to ion-mobility quadrupole time-of-flight mass spectrometry (UPLC-IMS-QTOF). *Talanta* **2024**, *266*, 124999. [CrossRef]
40. Aznar, M.; Domeño, C.; Nerín, C.; Bosetti, O. Set-off of non-volatile compounds from printing inks in food packaging materials and the role of lacquers to avoid migration. *Dyes Pigments* **2015**, *114*, 85–92. [CrossRef]
41. Vianna, T.C.; Gonçalves, S.D.A.; Marangoni Júnior, L.; Alves, R.M.V.; Andrade, V.T.; Sato, H.H.; Vieira, R.P. Incorporation of limonene oligomers into poly(itaconic acid)/starch blend films for antimicrobial and antioxidant packaging applications. *ACS Sustain. Chem. Eng.* **2024**, *12*, 8752–8764. [CrossRef]
42. Basak, S.; Annapure, U.S. Atmospheric pressure pin-to-plate cold plasma modification of high methoxyl apple pectin: Impact on functional properties. *J. Agric. Food Res.* **2022**, *9*, 100356. [CrossRef]