Journal of Applied Polymer Science

WILEY

Applied Polymer SCIENCE

RESEARCH ARTICLE OPEN ACCESS

Food Contact Compatibility of Bioplastic Materials Filled With Degradable Additives for Repeated-Use Food Applications

Emanuela Drago[1] | Cristina Moliner[1] | Alberto Lagazzo[1] | Margherita Pettinato[1] | Alessandro Alberto Casazza[1] | Elisabetta Finocchio[1] | Patrizia Perego[1] | Elisabetta Arato[1,2]

[1]Department of Civil, Chemical and Environmental Engineering (DICCA), University of Genoa, Genova, Italy | [2]Tecnologie Innovative Per IL Controllo Ambientale E Lo Sviluppo Sostenibile Scrl (TICASS), Genova, Italy

Correspondence: Cristina Moliner (cristina.moliner@unige.it)

Received: 6 November 2024 | **Revised:** 22 January 2025 | **Accepted:** 24 March 2025

Funding: This work has received funding from the European Union's Horizon 2020 Research and Innovation Programme through the research project BIO-PLASTICS EUROPE (grant agreement no. 860407).

Keywords: biocompatibility | biopolymers and renewable polymers | degradation | packaging

ABSTRACT

The packaging sector is the primary contributor to plastic waste due to the prevalence of disposable packaging. Although there is extensive literature on sustainable single-use packaging, studies on reusable biomaterials and their compliance with food contact regulations remain scarce. This study aimed to investigate the physicochemical properties of polylactic acid-based bioplastics reinforced with various degradable additives, glass fibers, and calcium carbonates, designed for repeated-use applications such as cutlery and rigid crates. All samples were tested for overall and specific migration in accordance with European Union regulations, and their material properties were analyzed. The results demonstrated that the tested materials provided overall migration values below the limits, although some instabilities did not provide them with full compliance. In terms of mechanical performance, cutlery samples exhibited a deterioration in mechanical properties after contact with food simulants, limiting their potential for repeated use. In contrast, rigid crates demonstrated high resistance to mechanical degradation, maintaining their properties over time.

1 | Introduction

In recent decades, the dependence on fossil-based plastics has steadily increased, contributing significantly to economic growth. In the 1950s, global plastic production was around 1.5 million tons per year. By 2050, this is projected to rise to 1800 million tons annually [1].

After nearly a century of using these advantageous synthetic materials, a serious environmental impact has emerged due to the increasing accumulation of plastics in the environment [2], posing risks to ecosystems as plastic waste degrades slowly into microplastic particles [3].

The packaging sector is the largest contributor to plastic waste [4], primarily because of single-use packaging. For example, most plastic cutlery (C) is made from non-biodegradable and environmentally harmful materials such as polypropylene and polystyrene [5]. Additionally, managing the environmental and health damage caused by fossil fuel exploitation costs millions of dollars each year [6], highlighting the urgent need for alternatives. As a result, actions have been taken worldwide to limit

plastic use [7]. In 2021, the European Union banned several single-use plastic products, including straws, C, and tableware, under EU Directive 2019/904 [8].

In response, research has focused on finding sustainable solutions, with biopolymers and bioplastics emerging as promising alternatives [9, 10]. From an environmental perspective, many studies have assessed the life cycle impacts of these materials, newer sustainable management solutions [11, 12] or their impact on the mechanical recycling of conventional plastics [13]. However, not enough research has been done to confirm the non-toxicity of bioplastic waste to living organisms. Among bioplastics, polylactic acid (PLA) is regarded as one of the most promising biodegradable polymers for both rigid and flexible packaging (Lagazzo et al. 2024). The U.S. Food and Drug Administration (FDA) recognizes PLA as safe for food contact, as its monomer, lactic acid, is a safe food preservative [14]. PLA is derived from renewable sources like starch, sugar, cassava, and sugar cane, which serve as substrates for microbial fermentation [15]. It is a thermoplastic aliphatic polyester [5] and currently the most widely used biopolymer in the packaging sector, with an annual production of 500,000 t [16]. Its popularity is growing due to its versatility and demand, making it suitable for items like trays and bottles. PLA is also gaining traction in other sectors, particularly biomedical applications due to its biocompatibility, as well as in electronics [17]. Furthermore, PLA can be processed using conventional methods such as injection molding and extrusion, which are commonly used for producing synthetic packaging materials like polyethylene, polyvinyl chloride, and polystyrene [18]. However, like most biopolymers, PLA tends to have inferior performance compared to traditional plastics, especially in terms of mechanical properties, due to its brittleness and limited thermal resistance [19].

To enhance these properties, biopolymers, like synthetic polymers, require additives such as plasticizers, UV filters, and antioxidants [15, 20]. Some authors have improved the competitiveness of PLA by incorporating inorganic fillers like talc, kaolin, and calcium carbonate, which help maintain a low cost for the composite material [21].

In another study, the gas barrier properties of PLA were improved by combining it with cellulose nanocrystals using extrusion blowing, creating a material suitable for preserving moisture-sensitive products like dry foods [22]. Monteiro Cesar Oyama et al. enhanced the elastic modulus of PLA films produced via injection molding by blending them with poly(3-hydroxybutyrate-co-3-hydroxyvalerate) reinforced with glassy carbon and graphene nanoplatelets [23]. A circular economy approach was demonstrated by Bezerra Lima et al. where the mechanical properties of highly biodegradable packaging films were improved by creating a composite material from PLA and starch derived from mango waste, filled with organic montmorillonite, using solvent casting [24]. However, most additives used in biopolymers are not chemically bonded to the polymer matrix, which means they can easily migrate into the environment, raising concerns about food safety [25]. Therefore, when designing new packaging materials, it is essential to meet not only mechanical and gas barrier requirements but also to comply with the European Commission regulations concerning materials intended for food contact, specifically in terms of overall and specific migration [26].

To the best of the authors' knowledge, whereas the literature is rich in studies on the production of innovative, especially disposable, materials and the enhancement of bioplastic properties, there is a notable lack of research focusing on the migration behavior of these bioplastics. Migration properties are crucial for materials designed for food contact, and their modification after use is a pivotal concern, especially for materials intended for repeated use.

In this study, the physicochemical properties of PLA-based bioplastics reinforced with degradable glass fibers and calcium carbonate were examined to assess their suitability for repeated-use applications such as C and for storing frozen fish and products kept at room temperature for extended periods. Compliance was evaluated based on overall and specific migration tests in line with European regulations. Additionally, mechanical and morphological analyses were conducted to investigate structural changes in the bioplastics after contact with food. This paper extends a previous study on biomaterials optimization conducted as part of the BIO-PLASTICS EUROPE project (https://bioplasticseurope.eu/), which aims to deliver sustainable strategies and solutions for bio-based plastics to support the EU Plastic Strategy [27].

2 | Materials and Methods

2.1 | Materials Description

PLA-based polymers filled with 20% by weight degradable glass fibers, provided by Arctic Biomaterials OY Ltd. (ABM, Finland), were designed for the production of multi-use C via injection molding. Additionally, PLA-based polymers (60% by weight) with calcium carbonate as a mineral filler (40% by weight) and also processed through injection molding were provided by Arctic Biomaterials OY Ltd. (ABM, Finland) for use as reusable rigid Fish Crates (FC). These crates are intended for the storage and transport of frozen fish, with an estimated shelf life of 1–2 years.

The bio-based plastics were tested using dumbbell-shaped test bars with dimensions of 74.5 mm in length and 2 mm in thickness. These samples were evaluated as part of the BIO-PLASTICS EUROPE project (Grant Agreement no. 860407).

The samples were labeled as C-X or FC-X, where "C" or "FC" indicates the sample type (C or fish crate), followed by a letter representing the simulant used in test conditions (X = A, B, or D2, according to European Commission regulations 1416 of 2016, to demonstrate compliance with the overall migration limit for all types of foodstuffs). In particular, simulant A corresponds to a hydroalcoholic mixture of ethanol 10% v/v to simulate foodstuffs of a hydrophilic character; simulant B is made up of an aqueous mixture of acetic acid 3% w/v to simulate foodstuffs of an acidic character with a pH below 4.5; simulant D2 adopted in this work corresponds to a hydroalcoholic solution of ethanol 95% v/v to simulate foodstuffs containing free fats in the surface that can

be used as a substitute simulant for vegetable oil as stated in the above-mentioned regulation. To compare the material properties before and after contact with food, reference materials, labeled C-ref and FC-ref, were also tested.

2.2 | Overall Migration Tests

The samples were subjected to overall migration tests by total immersion method according to the standard EN 1186–1 [28]. For each type of supplied material, test conditions were selected considering the most severe in terms of food simulant, exposure temperature, and contact time with the simulant. These parameters depend on the expected final application, according to the European regulations no 2020/1245 [29], which amends and rectifies reg. (EU) no 10/2011 [26] concerning plastic materials and objects intended to come into contact with food products. Based on the European regulations no 2020/1245 (L288/15), global migration testing for the conformity assessment of packaging materials for food both with hydrophilic and lipophilic character stored at frozen and refrigerated conditions for contact times longer than 30 days must be tested for 10 days at 20°C. In contrast, for any prolonged storage at room temperature or below, including heating up to 70°C for a duration of up to 2 h or heating up to 100°C for a duration of up to 15 min, the packaging material must be tested using food simulants for 10 days at 40°C. These standardized conditions specified by the regulation are in fact accelerated test conditions, that is they serve to have a higher migration in a shorter time than the expected final application.

Table 1 shows the details of the conditions adopted for the overall migration tests. All the experiments were performed in triplicate under controlled temperature conditions using an incubator chamber at 20°C and 40°C. Following the Italian Ministerial Decree of 21 March 1973, Annex IV (Determination of overall migration. Ministerial 21 March 1973, Annx IV, n.d.), the volume of the food simulant was evaluated to maintain the S/V ratio between the surface of the sample exposed to the simulant (cm^2) and the simulant volume (cm^3), constant and equal to 0.6. The surface of each sample was measured using the ImageJ software (NIH, Bethesda, MD, USA). As the packaging materials were intended for repeated use, reg. (EU) no 2020/1245 specifies that migration tests have to be conducted three times on the same sample, using fresh simulant each time. Therefore, tests on fish crates and C were performed accordingly, and samples coming from the first, second, and third stages of the test were labeled as round I, II, and III, respectively. Overall migration was assessed gravimetrically after complete drying of the simulant containing the migrated material at 105°C until constant weight was reached. All the experiments were performed in triplicate and the results were expressed as mean value ± standard deviation.

2.3 | Specific Migration Tests for Heavy Metals Detection

Specific migration tests (EN 13130) [30], for the detection of metal species (cobalt, chromium, iron, lithium, manganese, nickel, copper, and zinc), according to the procedures required by regulation (EU) no 2020/1245, which amends and rectifies reg. (EU) no 10/2011, were undertaken under the conditions of temperature and time reported in Table 1, but using 3% w/v acetic acid as food simulant (Simulant B), in agreement with the Italian Ministerial Decree of 21 March 1973, Annex IV, Section 7. Indeed, the simulant reproducing the most severe conditions was adopted. After the migration tests, liquid simulants were filtered (0.45 μm) and analyzed by an Atomic absorption spectrometer (Varian AA240Z, Markham, ON, Canada) equipped with a graphite furnace (GTA 120280) for the quantification of the metal species. All the experiments were performed three times, and the results were expressed as mean value ± standard deviation.

The specific migration values (MS) which expresses the mg of substance released by the packaging per kg of food or food simulant, must be corrected on the basis of the final surface area of the foodstuff to be packaged. In particular, for FC the results must be corrected using the experimental equation: $\text{MS finished product} = \frac{\text{MS sample} \times \text{Area finished product}}{0.173 \pm 0.004\ \text{dm}^2}$; and for C: $\text{MS finished product} = \frac{\text{MS sample} \times \text{Area finished product}}{0.175 \pm 0.003\ \text{dm}^2}$.

Descriptive statistical analyses for migration tests were carried out using the Statistica v 12.0 software (StatSoft, Tulsa, OK, USA).

TABLE 1 | Overall migration test conditions, correction coefficients, and limits reported by reg. (EU) no 10/2011 [26], and adopted in this study.

Materials	Simulant	Test conditions	Type of intended use	Correction coeff. (EU reg. 10/2011, Annex 5, Chapter 4)	Limit EU reg. 10/2011, art. 12 (mg/dm^2)
Fish crates	A = EtOH 10% v/v D2* = EtOH 95% v/v	10 days at 20°C (×3 times)	Repeated use (EU reg. 2020/1245. Annex 2. Chapter 3)	M/3 (only for D2* simulant)	10
Cutlery (C)	A = EtOH 10% v/v B = acetic acid 3% w/v D2* = EtOH 95% v/v	10 days at 40°C (×3 times)	Repeated use (EU reg. 2020/1245. Annex 2. Chapter 3)	None	10

Note: D2* indicates the use of the food simulant EtOH 95% v/v in place of vegetable oil containing less than 1% unsaponifiable substance.

2.4 | Mechanical Test

Static mechanical tests were obtained using an electro-mechanical universal testing machine Zwick/Roell Z50, equipped with a modular sensor arm extensometer makroXtens II and a load cell of 50 KN. The test was performed before and after migration tests to investigate any structural modifications due to their simulated repeated use. Tensile tests were performed according to the Standard DIN EN ISO 527-1 on dog-bone specimens at room temperature. All the tests were run with a rate of 1 mm/min for the determination of the Tensile Elastic Modulus and with a rate of 50 mm/min until break. The mechanical results obtained from these tests were: Tensile Young's Modulus, ultimate tensile strength (UTS), namely the maximum stress recorded during the test, Strain at UTS, Stress at breaking, and Strain at breaking.

2.5 | Scanning Electron Microscopy (SEM)

The morphological analysis was performed with a SEM Hitachi S-2500, in secondary electron mode. The analysis was conducted before and after migration tests to investigate any morphological changes due to their simulated repeated use. A portion of about 5 mm was obtained from the samples used for the tensile tests. The samples were observed, after gold coating, on the external surface at 100× and 500× magnifications.

2.6 | Fourier Transform Infrared Spectroscopy (FTIR-ATR)

FTIR-ATR spectra have been performed using a FT Nexus Thermo Nicolet instrument equipped with an ATR accessory (diamond window), 100 scans, 4 cm^{-1} resolution, DTGS detector, background air. Spectra were collected for all the samples in the range 4000–400 cm^{-1} (mid-IR region). Each analysis has been repeated on a different specimen or different points of the same sample.

3 | Results and Discussion

3.1 | Overall Migration Analysis

Overall migration tests were performed according to the conditions reported in Table 1, where also eventually adopted correction coefficients, defined by regulation (EU) no 10/2011, are indicated. Table 2 shows, for each material tested, the mean values of their overall migrations (M), for each round, expressed as mg of migrated material per dm^2 of sample surface, and the respective standard

TABLE 2 | Descriptive statistics on overall migration results obtained from tests on fish crates and C material samples.

Round	M [mg/dm²]	SD [mg/dm²]	I.C. −95% [mg/dm²]	I.C. +95% [mg/dm²]	Min [mg/dm²]	Max [mg/dm²]	Std. error [mg/dm²]	Limit EU reg. [mg/dm²]
Simulant A–fish crates 20°C–30 days								
I	3.70	0.57	2.28	5.12	3.04	4.10	0.33	—
II	1.24	0.32	0.43	2.04	0.87	1.46	0.19	—
III	0.52	0.29	0.00	1.25	0.30	0.85	0.17	10
Simulant D2*–fish crates 20°C–30 days[a]								
I	1.98	0.34	1.15	2.81	1.60	2.24	0.19	—
II	1.08	0.34	0.24	1.93	0.76	1.44	0.20	—
III	0.67	0.24	0.09	1.26	0.47	0.93	0.14	10
Simulant A–cutlery 40°C–30 days								
I	2.46	0.72	0.68	4.24	1.97	3.29	0.41	—
II	1.22	0.71	0.00	2.99	0.59	2.00	0.41	—
III	1.05	0.14	0.70	1.39	0.90	1.17	0.08	10
Simulant B–cutlery 40°C–30 days								
I	25.48	10.02	0.58	50.37	17.08	36.57	5.79	—
II	3.29	2.15	0.00	8.63	0.92	5.11	1.24	—
III	2.12	0.34	1.28	2.95	1.73	2.32	0.19	10
Simulant D2*–cutlery 40°C–30 days								
I	22.63	3.11	14.89	30.36	20.33	26.17	1.80	—
II	5.94	1.31	2.67	9.20	4.76	7.36	0.77	—
III	3.41	1.91	0.00	8.15	1.81	5.52	1.10	10

Note: Results are reported as mean value of migration (M = mg of migrated material per dm^2 of sample area) and its standard deviation (SD). Results obtained by the descriptive statistical analysis are expressed as interval of confidence (I.C.), minimum and maximum values (Min, Max) and standard error (Std. error). Simulant A: EtOH 10% v/v; simulant B: Acetic acid 3% w/v; simulant D2*: EtOH 95% v/v.

[a]Results were corrected by the correction coefficient (M/3) defined by the EU regulation (EU reg. 1416/2016).

deviations (SD), confidence intervals (I.C.), minimum and maximum values (Min, Max), and standard errors obtained from the descriptive statistical analysis. In agreement with reg. (EU) no 10/2011 [26], Art. 12 on materials intended for repeated use, the simulant collected during the third test (III round) was used to verify compliance with the limits of migration. Furthermore, the decreasing level of overall migration detected in the first, second, and third tests, respectively, was verified, as required by the regulation.

Both the releases from FC samples into simulants A and D2* exhibited lower concentrations of migrated material moving from round I to round III (Table 2). Furthermore, mean MS of the last rounds (III) always lay under the limits indicated by the EU regulation (10 mg/dm^2), as well as the maximum experimental values detected. For completeness, the mean concentrations of the II and I runs were verified to be lower than the limit established by regulations, even if such limit is actually referred to the last round for repeated-use materials. Therefore, based on the obtained results, these materials could be used as packaging for food both with hydrophilic and lipophilic character stored at frozen and refrigerated conditions for contact times longer than 30 days. Similarly, the results of the global migration of C showed that this material also complied with the relevant global migration limits (Table 2), as the MS attributed to round III were always below the imposed limits and a decreasing migration value was found for all simulants tested round after round. However, as the migration of round I exceeded the regulatory limits, it is not possible to ascertain the stability of this material for use in contact with all types of food stored at room temperature or below and heated up to 70°C for up to 2 h or up to 100°C for up to 15 min. Therefore, further evaluation and modification of the formulated material will be necessary.

3.2 | Specific Migration Analysis

Table 3 shows the specific MS, expressed as mg of metal migrated per kg of simulant, from the FC samples after tests conducted for 30 days at 20°C in 3% w/v acetic acid. The mean concentration of all the metals, except chromium, was recorded to be under the EU regulation limits. This result was also demonstrated by the maximum values (Max) and the confidence intervals (I.C.), deriving from the descriptive statistical analysis.

Regarding FC samples, albeit the mean concentration of Cr was lower than the limit, a high standard deviation (SD) was associated, and the maximum experimental value was higher than the limit set at 0.01 mg/kg.

Table 3 shows also values of the specific migration from the C samples after tests conducted for 30 days at 40°C in 3% w/v acetic acid. The mean concentration of all the metals was recorded to be particularly under the EU regulation limits. This result was also remarked by the maximum experimental values (Max) observed and the confidence intervals (I.C.).

TABLE 3 | Descriptive statistics about results of specific migration of metal species into the simulant of the III round of tests.

Metal	MS [mg/kg]	SD [mg/kg]	I.C. −95% [mg/kg]	I.C. +95% [mg/kg]	Min [mg/kg]	Max [mg/kg]	Std. error [mg/kg]	EU reg. limit [mg/kg]
Fish crates–30 days (repeated use) at 20°C in 3% w/v acetic acid								
Co	0.0007	0.0015	0.0000	0.0019	0.0000	0.0046	0.0005	0.05
Cr	0.0084	0.0121	0.0000	0.0177	0.0032	0.0405	0.0040	0.01
Cu	0.0028	0.0017	0.0015	0.0042	0.0011	0.0061	0.0006	5
Fe	0.0453	0.0149	0.0339	0.0567	0.0310	0.0676	0.0050	48
Li	0.0008	0.0002	0.0006	0.0010	0.0006	0.0013	0.0001	0.6
Mn	0.0146	0.0021	0.0130	0.0162	0.0131	0.0191	0.0007	0.6
Ni	0.0074	0.0026	0.0055	0.0094	0.0052	0.0114	0.0009	0.02
Zn	0.1159	0.1217	0.0224	0.2094	0.0000	0.3219	0.0406	5
Cutlery-30 days (repeated use) at 40°C in 3% w/v acetic acid								
Co	< 0.005	—	—	—	—	—	—	0.05
Cr	0.0033	0.0002	0.0031	0.0034	0.0029	0.0036	0.0001	0.01
Cu	0.0038	0.0011	0.0029	0.0047	0.0018	0.0055	0.0004	5
Fe	0.0583	0.0108	0.0493	0.0673	0.0400	0.0671	0.0038	48
Li	0.0001	0.0001	0.0000	0.0001	0.0000	0.0003	0.0000	0.6
Mn	0.0046	0.0013	0.0035	0.0057	0.0026	0.0070	0.0004	0.6
Ni	0.0075	0.0014	0.0064	0.0086	0.0059	0.0096	0.0005	0.02
Zn	0.5137	0.3486	0.2457	0.7816	0.2480	1.0057	0.1162	5

Note: Results are reported as mean concentration of the metal and standard deviation (SD). Results obtained by the descriptive statistical analysis are expressed as interval of confidence (I.C.), minimum and maximum values (Min, Max) and standard error (Std. error).

3.3 | Mechanical Test

Both FC and C samples exhibit stress versus strain curves typical of rigid materials (Figure 1), with elongation at break values of 2% for the FC samples and 1% for the C samples, and no presence of a plastic plateau.

Immersion of the FC material in 10% and 95% ethanol, as well as in acetic acid, did not result in significant changes in mechanical behavior compared to the reference material. There was a moderate reduction in strain at break, from 2.2% to 1.8%, and a slight decrease in UTS, from 47 to 43 MPa. The Young's Modulus showed only negligible changes, ranging from 4.9 to 5.1 GPa.

A more pronounced effect was observed in the C samples, which exhibited material embrittlement after immersion in the simulants. The strain at break was halved, and there was a significant reduction in UTS, from 76 MPa in the reference samples (C-ref) to 43 MPa in samples immersed in 95% ethanol (C-D2), 30 MPa in those immersed in 10% ethanol (C-A), and 26 MPa in samples immersed in 3% acetic acid (C-B).

The Young's modulus also decreased, from 6 GPa (C-ref) to 3.9 and 3.6 GPa for samples immersed in 10% ethanol and 3% acetic acid, respectively. However, immersion in 95% ethanol had little effect on the elastic modulus, which remained at 5.9 GPa. This effect is likely due to the action of the water-ethanol solutions, which caused slight swelling and limited hydrolysis of the polymer, leading to a rearrangement of the molecular structure into a more crystalline conformation, as reported by other authors [31]. Although no specific data have been reported for acetic acid solutions, the high water content in simulants A and B may accelerate the recrystallization process, potentially explaining the observed changes in mechanical behavior.

3.4 | Morphology Characterization

The reference FC samples (FC-ref) show a smooth surface (Figure 2), with exposed fibers approximately 20 μm in diameter at the points of fracture. Rounded particles with irregular edges are visible in all FC samples, particularly in the FC-A samples, where these particles are more prominent and emerge from the bulk. Similarly, for the C samples (Figure 3), the external surface appears smooth, with rounded and irregular particles ranging from 10 to 30 μm in size. In the C-A samples, these particles are fully incorporated into the bulk, without noticeable increase in surface roughness that led to no physical disruptions, as described in others works on the degradation of PLA composites [32]. In the C-B and C-D2 samples, instead, particles emerge from the surface, likely due to the degradation and dissolution of the polymeric matrix's outer layer. The presence of irregular rounded particles that emerge from the surface was already observed as an effect of the alcohol solution on the PLA samples, in which circular flakes partially detached are evident [27].

The observed morphological changes after immersion in the simulants appear to be limited to the external surface and do not necessarily induce changes in mechanical behavior. Instead, the mechanical properties are more likely affected by alterations occurring throughout the bulk of the material.

3.5 | FTIR-ATR Studies

FTIR-ATR analysis has been applied in order to characterize any possible changes in the polymer's main functional groups structure before and after the migration tests described above [27].

The IR spectrum of the reference FC sample (FC-ref) shows a main band with two sharp maxima centered at 1715 and 1755 cm^{-1} and assigned to vC═O of ester groups in the polymer structure (Figure 4a). Namely, the latter component is completely consistent with the vC═O band in pure PLA material. The complex absorption with maxima at 1180, 1158, 1130, 1085, 1045 cm^{-1} is due to C—O—C and CC stretching modes of the ester group with some contribution of CH deformation of the CH_3 group, whereas weaker bands in the region 1450–1330 cm^{-1} are assigned to CH deformation modes [33]. Moreover, a broad absorption appears to be overlapped with the polymer bands, increasing the overall IR baseline absorption below the peaks in the region 1500–1300 cm^{-1}, and assignable to the carbonate group of calcium carbonate inorganic filler, together with the sharp component near 870 cm^{-1}.

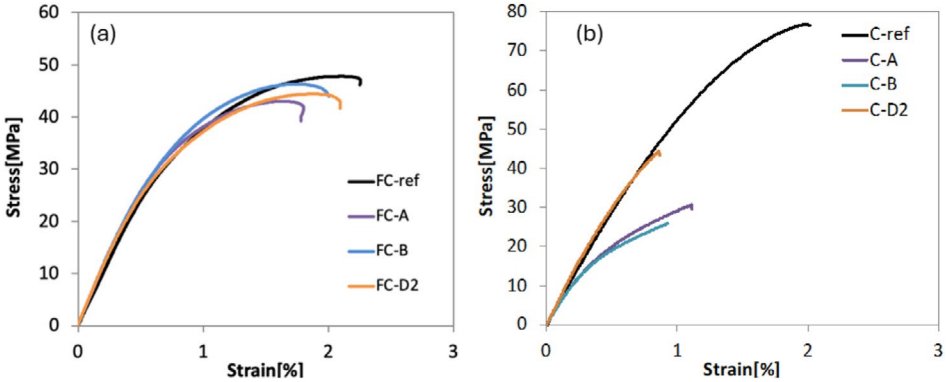

FIGURE 1 | Comparison of stress versus strain plots obtained with tensile test on (a) fish crates (FC samples); and on (b) Cutlery samples (C samples). [Color figure can be viewed at wileyonlinelibrary.com]

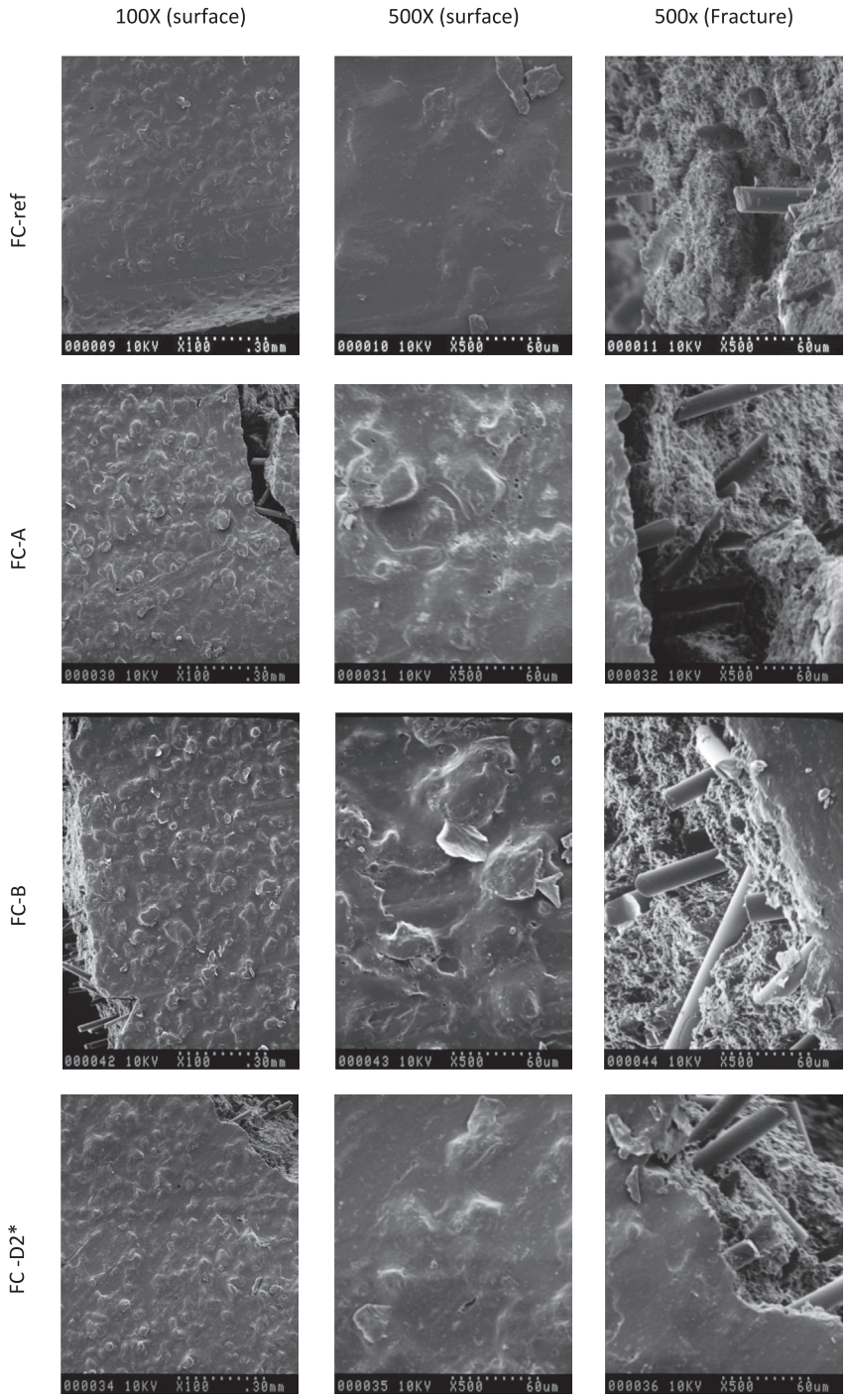

FIGURE 2 | SEM images at ×100, ×500 on the external surface and on the fracture of the samples FC subjected to different treatments.

In the spectra of samples after treatments in ethanol (10% v/v FC-A and 95% v/v FC-D2), the bands characterizing the ester groups do not show significant variations in comparison to bands of the pristine FC-ref sample (Figure 4a). CH deformation modes of the polymer chain are completely consistent, too (Figure 4b). On the other hand, after treatment in acetic acid at 20°C (FC-B), bands in the region 1500–1350 cm^{-1} become less intense and sharper than in the previous case, and the mentioned broad absorption underneath the polymer features disappears. In parallel, the relative intensity of the band at 870 cm^{-1} decreases. These results suggest that the carbonate species are decomposed at least partially in the acidic medium. Weak absorptions appear at 1615 and 1545 cm^{-1}, which could be related to the formation of new exposed functional groups whose assignation is not straightforward (inset in Figure 4a). In the high frequency region of the spectrum, after treatment in acetic acid, a very weak and broad additional absorption is present in the range 3500–3400 cm^{-1}, that could be assigned to stretching modes of new exposed hydroxyl groups (Figure 4b).

The comparison of the spectra indicated that after treatments in ethanol simulants, bands of the FC polymer structure are detected almost unchanged. Thus, spectroscopic data do not evidence a relevant formation of free carboxylic and hydroxyl

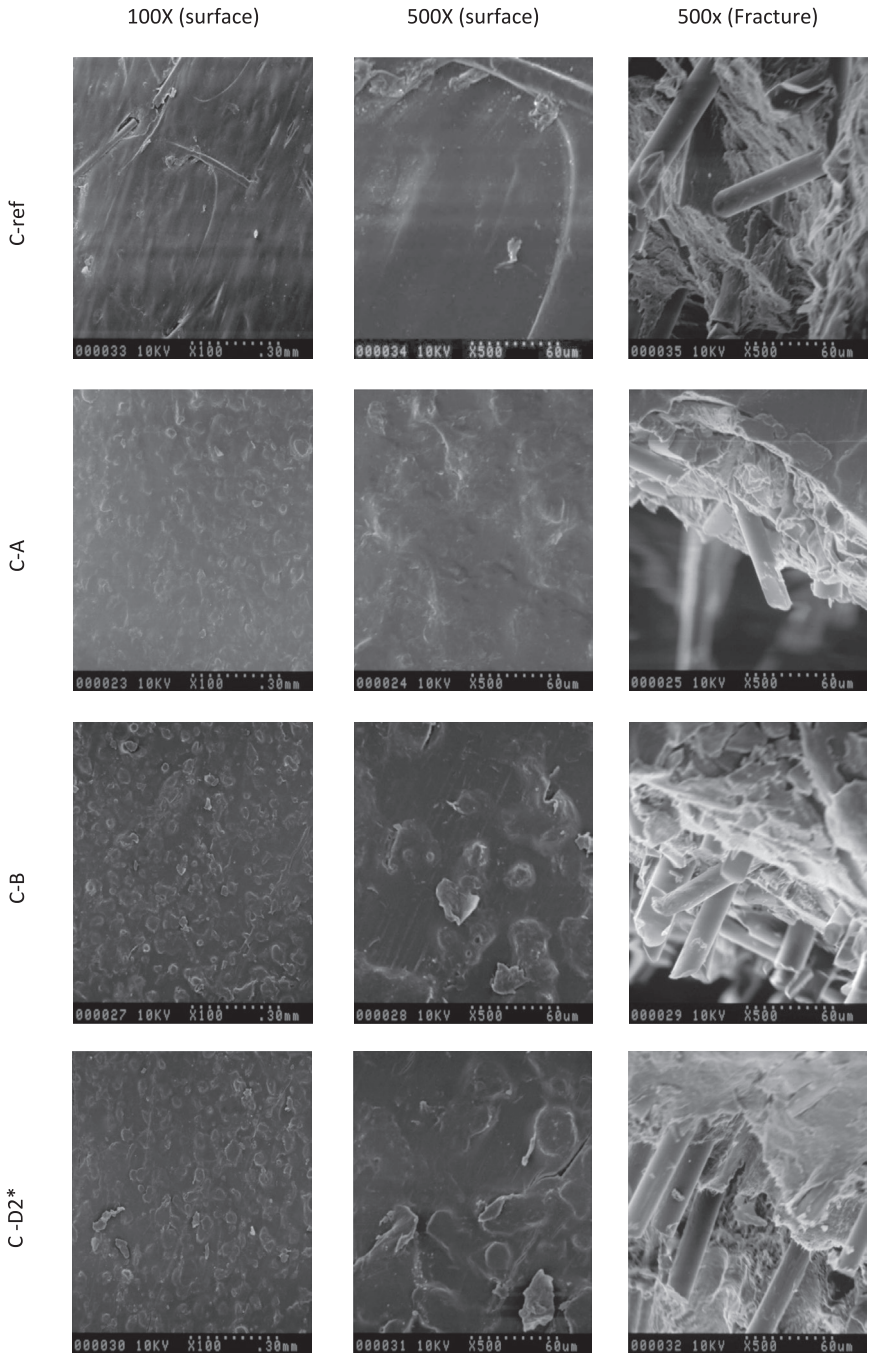

FIGURE 3 | SEM images at ×100, ×500 on the external surface and on the fracture of the samples C subjected to different treatments.

groups that should be expected after a massive cleavage by hydrolysis of the ester bonds in the polymer chains. These results are consistent with the similar mechanical behavior of the samples reported in Section 3.3. Only the acidic medium leads to some changes which, however, appear to be mostly due to the loss of some additional components of the material formulation. The formation of some free carboxylic groups at the ends of the polymer chain is also possible, as suggested by the increase of relative intensity of the band at 1715 cm^{-1}. In Figure 5, the IR spectrum of the reference C material shows the same set of bands described above for sample FC, having a common PLA-based structure. In sum, a main band centered at 1714 cm^{-1}, with a component at 1755 cm^{-1}, is assigned to vC═O of the ester group in the PLA structure, the complex absorption in the range 1200–1050 cm^{-1} due to C—O—C and CC stretching modes, bands in the region 1450–1330 cm^{-1} assigned to CH deformation modes. The low frequency region of the spectra does not evidence any significant change in shape or position of the main bands following the treatments in aqueous solutions of either ethanol (10 and 95% v/v) or acetic acid 3% w/v, thus suggesting that hydrolysis of the samples in our conditions is limited.

Therefore, at the highest temperature used in this study, the polymer functional groups appear not to be affected by the treatments in ethanol and acetic acid. Only in the high frequency region of the spectra some differences can be detected, namely two sharp bands at 2917 and 2849 cm^{-1} (CH stretching modes)

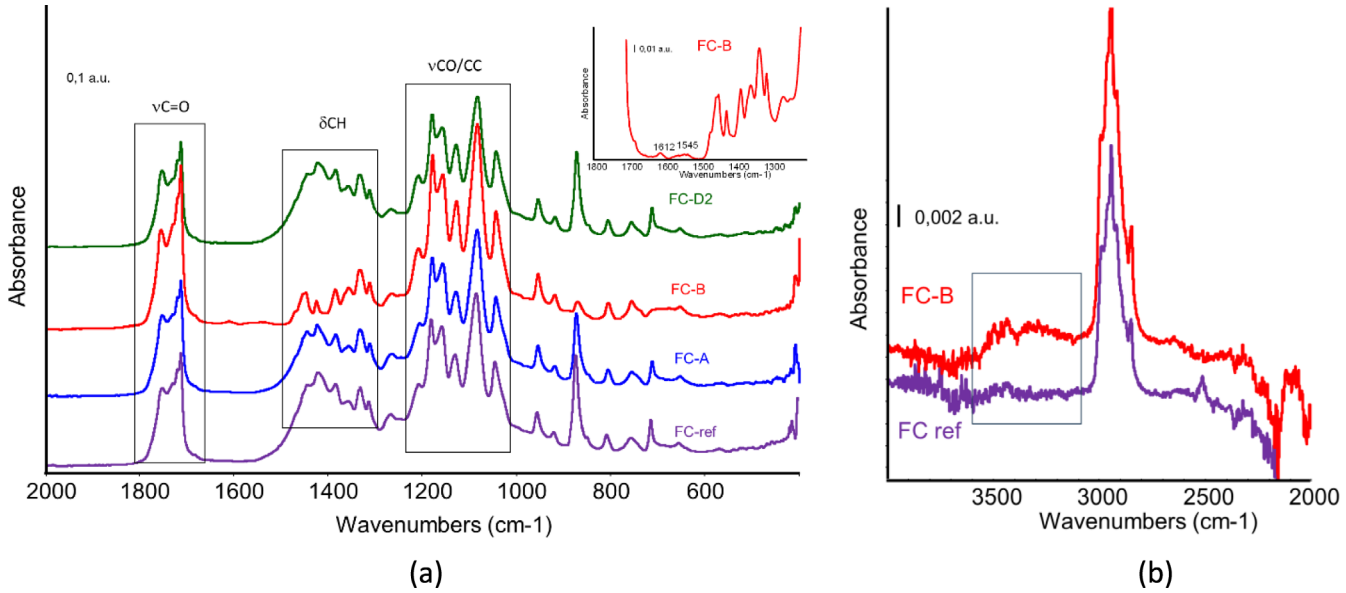

FIGURE 4 | (a) ATR IR spectra of samples FC in the mid-IR spectral region (not treated reference sample: Spectrum FC-ref); (b) ATR IR spectra of samples FC in the range 3500–3400 cm^{-1}. Inset: Enlargement of spectrum FC-B. [Color figure can be viewed at wileyonlinelibrary.com]

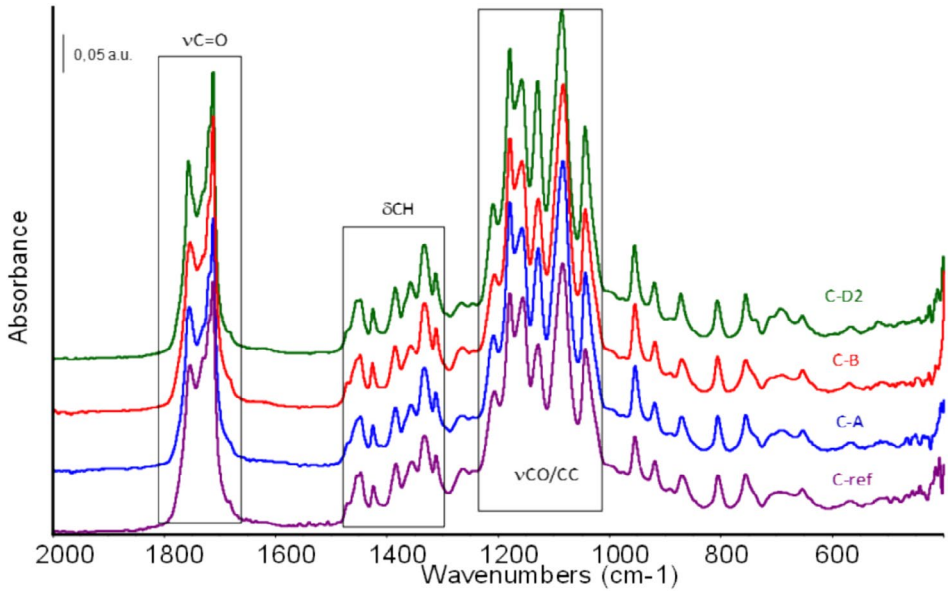

FIGURE 5 | ATR IR spectra of samples C in the mid-IR spectral region (reference spectrum C-ref). [Color figure can be viewed at wileyonlinelibrary.com]

for samples C-A and C-B, and that can be due to the inclusion of some residual ethanol or acid molecules in the layers.

3.6 | Discussion

The biomaterials fabricated for use as FC were analyzed through overall migration tests, conducted at 20°C for 30 days in simulants A (10% v/v ethanol) and D2* (95% v/v ethanol). The results obtained were in accordance with the regulatory limits for repeated-use materials. Specific migration tests performed in simulant B under the same temperature and time conditions showed values within the specific limits, with the exception of chromium detected in only one specimen. Mechanical properties were maintained even after immersion in 10% and 95% v/v ethanol, and FTIR-ATR analysis indicated very limited chemical changes induced by solvent exposure [34]. Therefore, the Fish Crate material appears suitable for the investigated application involving frozen and refrigerated food products, whether hydrophilic or lipophilic in nature. Furthermore, the presence of calcium carbonate as an additive likely contributed to the stabilization of the PLA-based material, considering the differing mechanical results observed for the C materials discussed below.

For the C biomaterials, overall migration tests were conducted at 40°C for 30 days in simulants A (10% v/v ethanol), B (3% w/v acetic acid), and D2* (95% v/v ethanol), resulting in values

below the regulatory limits, but tests showed insufficient stability of the samples to guarantee full migration compliance. Furthermore, specific migration tests in simulant B under the same conditions yielded values within the limits. However, the evaluation of mechanical properties indicated embrittlement of the C samples after migration tests, which could limit their applications, particularly for hydrophilic food products, as they exhibited the highest fragility post-migration simulating repeated use. These changes in mechanical behavior may be attributed to hydrolytic degradation of the polymer, swelling induced by the water fraction in the simulants, and concurrent solvent-induced crystallization, as previously reported by other authors after exposing PLA disks to ethanol/water mixtures at 40°C [31, 35]. In this study, the very similar IR spectra observed for the series of C samples compared to the pristine material spectra suggest that hydrolytic phenomena are not particularly significant, as bands associated with ester groups remained stable and clearly detectable following exposure to ethanol and acetic acid. On the other hand, the recrystallization process is possible, as indicated by the mechanical behavior. Finally, the C material does not meet all migration limits, being unsuitable for repeated use and requiring further study.

All reported results for specific migration are specific to the test conditions adopted and are influenced by the surface area of the supplied samples exposed to the simulants. Therefore, for each intended application, it is essential to apply the correction factors noted below the tables in relation to the exposed surfaces of the final product.

In summary, whereas literature is rich in studies on the production of innovative, especially disposable, materials and the enhancement of bioplastic properties, this study focused on addressing plastic waste through reusable biomaterials compliant with food contact regulations. As shown, PLA-based materials show great potential, but still research needs to be done to achieve a highly optimized and competitive solution.

4 | Conclusions

Polylactic acid rigid packaging provides an eco-friendly alternative to traditional plastics, supporting sustainable packaging goals. The materials investigated in this work show promising potential for use in the food industry, meeting essential safety standards for both hydrophilic and lipophilic products. This study explored the applicability of two types of PLA packaging reinforced with mineral and degradable additives.

The materials designed for FC met all regulatory limits concerning overall migration. However, a specific concern arose regarding chromium migration, as only one sample in repeated tests exhibited a high value, which is considered an isolated case. Mechanical tests and FTIR-ATR analysis confirmed the mechanical and chemical stability of the polymer structure of these materials after repeated use. In contrast, the C material demonstrated compliance with the migration limits, but its stability could not be guaranteed, which also exhibited increased brittleness upon repeated use. This brittleness can be explained by a limited hydrolytic degradation of the surface ester bonds, as suggested by FTIR-ATR analysis. This will lead to some rearrangement of the polymer chain structures and to increased crystallinity of PLA following contact with simulants at high aqueous content. Therefore, prolonged use of this material for hydrophilic foods is not recommended.

Author Contributions

Emanuela Drago: formal analysis (lead), investigation (lead), writing – original draft (lead). **Cristina Moliner:** investigation (equal), methodology (equal), writing – review and editing (equal). **Alberto Lagazzo:** investigation (equal), methodology (equal), writing – review and editing (equal). **Margherita Pettinato:** investigation (equal), methodology (equal). **Alessandro Alberto Casazza:** methodology (supporting). **Elisabetta Finocchio:** investigation (equal), methodology (equal), writing – review and editing (equal). **Patrizia Perego:** supervision (equal). **Elisabetta Arato:** funding acquisition (lead), supervision (lead), writing – review and editing (equal).

Acknowledgments

Open access publishing facilitated by Universita degli Studi di Genova, as part of the Wiley - CRUI-CARE agreement.

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

Data will be made available by the authors upon reasonable request.

References

1. N. A. A. B. Taib, M. R. Rahman, D. Huda, et al., "A Review on Poly Lactic Acid (PLA) as a Biodegradable Polymer," *Polymer Bulletin* 80, no. 2 (2023): 1179–1213, https://doi.org/10.1007/s00289-022-04160-y.

2. N. Mhaddolkar, T. F. Astrup, A. Tischberger-Aldrian, R. Pomberger, and D. Vollprecht, "Challenges and Opportunities in Managing Biodegradable Plastic Waste: A Review," *Waste Management & Research: The Journal for a Sustainable Circular Economy* (2024): 1–24, https://doi.org/10.1177/0734242X241279902.

3. D. Dordevic, L. Necasova, B. Antonic, S. Jancikova, and B. Tremlová, "Plastic Cutlery Alternative: Case Study With Biodegradable Spoons," *Food* 10, no. 7 (2021): 1612, https://doi.org/10.3390/foods10071612.

4. S. Rhein and M. Schmid, "Consumers' Awareness of Plastic Packaging: More Than Just Environmental Concerns," *Resources, Conservation and Recycling* 162 (2020): 105063, https://doi.org/10.1016/j.resconrec.2020.105063.

5. M. Basil, M. K. Anirudh, A. N. Lal, M. P. Harikrishnan, P. Kundu, and A. Kothakota, "Development and Characterization of Microfiber Incorporated With Industrial Biopolymer Composite Based Biodegradable Cutlery: An Alternative to Single Use Plastic," *Industrial Crops and Products* 205 (2023): 117526, https://doi.org/10.1016/j.indcrop.2023.117526.

6. J. Gao, Y. Wu, J. Li, et al., "Toughening and Heat-Resistant Modification of Degradable PLA/PBS-Based Composites by Using Glass Fiber/Silicon Dioxide Hybrid Fillers," *Polymers* 14, no. 16 (2022): 3237, https://doi.org/10.3390/polym14163237.

7. B. Jiang, J. Yu, and Y. Liu, "The Environmental Impact of Plastic Waste," *Journal of Environment and Earth Science* 2, no. 2 (2020): 26–35, https://doi.org/10.30564/jees.v2i2.2340.

8. Y. Miele, G. Esposito, M. Ricciardi, et al., "Multiuse Polystyrene Plates for Phasing out Single-Use Plastics: Chemical Performances and

Environmental Impact Assessment Through a Life Cycle Approach," *Advanced Energy and Sustainability Research* 5, no. 7 (2024): 2300224, https://doi.org/10.1002/aesr.202300224.

9. E. Drago, P. Franco, R. Campardelli, I. De Marco, and P. Perego, "Zein Electrospun Fibers Purification and Vanillin Impregnation in a One-Step Supercritical Process to Produce Safe Active Packaging," *Food Hydrocolloids* 122 (2022): 107082, https://doi.org/10.1016/j.foodhyd.2021.107082.

10. N. M. Stark and L. M. Matuana, "Trends in Sustainable Biobased Packaging Materials: A Mini Review," *Materials Today Sustainability* 15 (2021): 100084, https://doi.org/10.1016/j.mtsust.2021.100084.

11. F. Marchelli, M. Mattonai, R. Ferrentino, et al., "Fostering Bioplastics Circularity Through Hydrothermal Treatments: Degradation Behavior and Products," *ACS Sustainable Chemistry & Engineering* 12, no. 24 (2024): 9257–9267, https://doi.org/10.1021/acssuschemeng.4c02174.

12. G. Ischia, F. Marchelli, N. Bazzanella, et al., "Cellulose Acetates in Hydrothermal Carbonization: A Green Pathway to Valorize Residual Bioplastics," *ChemSusChem* 18, no. 2 (2025): e202401163, https://doi.org/10.1002/cssc.202401163.

13. M. J. Staplevan, A. J. Ansari, A. Ahmed, and F. I. Hai, "Impact of Bioplastic Contamination on the Mechanical Recycling of Conventional Plastics," *Waste Management* 185 (2024): 1–9, https://doi.org/10.1016/j.wasman.2024.05.028.

14. T. A. Swetha, A. Bora, K. Mohanrasu, et al., "A Comprehensive Review on Polylactic Acid (PLA)–Synthesis, Processing and Application in Food Packaging," *International Journal of Biological Macromolecules* 234 (2023): 123715, https://doi.org/10.1016/j.ijbiomac.2023.123715.

15. M. Pettinato, M. Bolla, R. Campardelli, G. Firpo, and P. Perego, "Potential Use of PLA-Based Films Loaded With Antioxidant Agents From Spent Coffee Grounds for Preservation of Refrigerated Foods," *Food* 12, no. 22 (2023): 4167, https://doi.org/10.3390/foods12224167.

16. European Bioplastics, "Bioplastics Market Development Update 2024," 2025, https://Www.European-Bioplastics.Org/Market/.

17. R. Donate, M. Monzón, and M. E. Alemán-Domínguez, "Additive Manufacturing of PLA-Based Scaffolds Intended for Bone Regeneration and Strategies to Improve Their Biological Properties," *E-Polymers* 20, no. 1 (2020): 571–599, https://doi.org/10.1515/epoly-2020-0046.

18. R. A. Ilyas, S. M. Sapuan, M. M. Harussani, M. Y. A. Y. Hakimi, M. Z. M. Haziq, and M. S. N. Atikah, "Polylactic Acid (PLA) Biocomposite: Processing, Additive Manufacturing and Advanced Applications," *Polymers* 13, no. 8 (2021): 1326, https://doi.org/10.3390/polym13081326.

19. C. Moliner, J. D. Badia, B. Bosio, et al., "Thermal Kinetics for the Energy Valorisation of Polylactide/Sisal Biocomposites," *Thermochimica Acta* 670 (2018): 169–177, https://doi.org/10.1016/j.tca.2018.10.029.

20. M. Z. Mulla, M. R. T. Rahman, B. Marcos, B. Tiwari, and S. Pathania, "Poly Lactic Acid (Pla) Nanocomposites: Effect of Inorganic Nanoparticles Reinforcement on Its Performance and Food Packaging Applications," *Molecules* 26, no. 7 (2021): 1967, https://doi.org/10.3390/molecules26071967.

21. K. Helanto, R. Talja, and O. J. Rojas, "Effects of Talc, Kaolin and Calcium Carbonate as Fillers in Biopolymer Packaging Materials," *Journal of Polymer Engineering* 41, no. 9 (2021): 746–758, https://doi.org/10.1515/polyeng-2021-0076.

22. S. S. Karkhanis, N. M. Stark, R. C. Sabo, and L. M. Matuana, "Potential of Extrusion-Blown Poly(Lactic Acid)/cellulose Nanocrystals Nanocomposite Films for Improving the Shelf-Life of a Dry Food Product," *Food Packaging and Shelf Life* 29 (2021): 100689, https://doi.org/10.1016/j.fpsl.2021.100689.

23. I. M. C. Oyama, E. G. R. dos Anjos, G. F. de Melo Morgado, T. R. Brazil, M. C. Kantun-Uicab, and F. R. Passador, "Preparation of Antistatic and Biodegradable Packaging of PLA/PHBV Blend-Based Glassy Carbon and Graphene Nanoplatelets Composites," *Journal of Applied Polymer Science* 141, no. 7 (2024): e54952, https://doi.org/10.1002/app.54952.

24. E. M. B. Lima, A. M. Lima, A. P. S. Minguita, et al., "Poly(Lactic Acid) Biocomposites With Mango Waste and Organo-Montmorillonite for Packaging," *Journal of Applied Polymer Science* 136, no. 21 (2019): 47512, https://doi.org/10.1002/app.47512.

25. F. Akoueson, I. Paul-Pont, K. Tallec, et al., "Additives in Polypropylene and Polylactic Acid Food Packaging: Chemical Analysis and Bioassays Provide Complementary Tools for Risk Assessment," *Science of the Total Environment* 857, no. Pt 2 (2023): 159318, https://doi.org/10.1016/j.scitotenv.2022.159318.

26. European Commission, "Regulation (EU) No. 10/2011 of 14 January 2011 on Plastic Materials and Articles Intended to Come Into Contact With Food," 2011.

27. E. Finocchio, C. Moliner, A. Lagazzo, S. Caputo, and E. Arato, "Water Absorption Behavior and Physico-Chemical and Mechanical Performance of PLA-Based Biopolymers Filled With Degradable Glass Fibers," *Journal of Applied Polymer Science* 140, no. 43 (2023): e54578, https://doi.org/10.1002/app.54578.

28. European Standards, "Materials and Articles in Contact With Foodstuffs–Plastics–Part 1: Guide to the Selection of Conditions and Test Methods for Overall Migration. British Standards BS EN 1186-1:2002. 49," 2002.

29. European Commission, "Regulation (EU) 2020/1245 of 2 September 2020 Which Modified Regulation n.10/2011 on Plastic Materials and Articles Intended to Come Into Contact With Food," *Gazzetta Ufficiale Dell'unione Europea* 16, no. 2 (2020): 1–17.

30. European Standards, "Materials and Articles in Contact With Foodstuffs—Plastics Substances Subject to Limitation—Part 2: Determination of Terephthalic Acid in Food Simulants (ISO-13130-2:2004)," 2004, British Standards BS EN 13130-1: 2004, 3.

31. F. Iñiguez-Franco, R. Auras, G. Burgess, et al., "Concurrent Solvent Induced Crystallization and Hydrolytic Degradation of PLA by Water-Ethanol Solutions," *Polymer* 99 (2016): 315–323, https://doi.org/10.1016/j.polymer.2016.07.018.

32. M. Ajmal, M. Asad, W. Huo, Y. Shao, and W. Lu, "Enhancing Degradation of PLA-Made Rigid Biodegradable Plastics With Non-Thermal Plasma Treatment," *Journal of Cleaner Production* 479 (2024): 143985, https://doi.org/10.1016/j.jclepro.2024.143985.

33. G. Kister, G. Cassanas, and M. Vert, "Effects of Morphology, Conformation and Configuration on the IR and Raman Spectra of Various Poly(Lactic Acid)s," *Polymer* 39, no. 2 (1998): 267–273, https://doi.org/10.1016/S0032-3861(97)00229-2.

34. S. Sato, D. Gondo, T. Wada, S. Kanehashi, and K. Nagai, "Effects of Various Liquid Organic Solvents on Solvent-Induced Crystallization of Amorphous Poly (Lactic Acid) Film," *Journal of Applied Polymer Science* 129, no. 3 (2013): 1607–1617, https://doi.org/10.1002/app.38833.

35. D. Xu, R. A. Auras, U. Sonchaeng, M. Rubino, and L. T. Lim, "The Effect of Alcoholic Solutions on the Thermomechanical Properties of Immersed Poly(Lactic Acid) Films," *Journal of Applied Polymer Science* 140, no. 11 (2023): e53489, https://doi.org/10.1002/app.53489.