

Biobased Polymer Recycling: A Comprehensive Dive into the Recycling Process of PLA and Its Decontamination Efficacy

Robert Paiva, Margarita Aznar, Magdalena Wrona, Ana Paula de Lima Batista, Cristina Nerín, and Sandra A. Cruz*



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ABSTRACT: The recycling process and the presence of contaminants play important roles in alimentary security. In this research, poly(lactic acid) (PLA) samples were contaminated using an FDA-defined framework by immersing them in a cocktail of five surrogates (benzophenone, tetracosane, heptane, chloroform, and toluene). Migration tests were then conducted on the samples after different recycling stages by using two food simulants and varying conditions. To this end, it was used SPME–GC–MS and GC–MS techniques in order to evaluate the efficiency of the recycling technology. The contaminants in PLA samples decreased after they were submitted to the total recycling cycle. Compounds such as tetracosane, heptane, and toluene showed decreased values between 73 and 80%, much higher than those obtained when the sample went through only washing or mechanical recycling. The theoretical molecular volume of contaminants, the type of food simulants, the temperature of the test, and the interactions between the polymer and surrogates influence the input and output of contaminants. The interaction energy values estimated from electronic structure calculations prove to be useful for predicting and analyzing global interaction trends between contaminants and the polymer. Consistency was observed between the results obtained from the Hansen sphere analysis and the theoretical approach.

KEYWORDS: PLA, biobased polymer, recycling, decontamination efficiency, SPME–GC–MS, quantum chemical calculations



1. INTRODUCTION

Efforts to substitute traditional plastic materials with those derived from renewable resources have gained prominence due to the environmental impact caused by the improper disposal of plastic products. Since the 1950s, the establishment of the polymer and plastics processing industry has contributed to improving the quality of society in areas ranging from textiles to food packaging or hospitals.¹ According to Leal Filho et al. and the Plastic Atlas data, packaging accounts for 50% of the annual production of plastic products, which has overtaken other industries during the COVID-19 pandemic due to the increase in the use of single-use plastic materials.^{2,3} However, plastic packaging accumulation and improper disposal are increasing over time, and reuse opportunities and environmental protection policies are not keeping pace with production and consumption.^{3,4}

The European Commission has published new directives to minimize impact, promote a culture of environmental responsibility, and facilitate the implementation of the circular economy to reduce nonrenewable resources to produce single-use packaging until their total elimination/exchange for materials from renewable sources. In addition, the new guidelines aim to promote the use of recycled raw materials

and include the use of biodegradable biobased polymers in manufacturing plastic packaging.^{5,6}

The use of biobased polymers from renewable sources is an essential alternative for reducing environmental concerns, mainly because it reduces the dependence on petroleum-based materials.⁷ However, the problem of accumulation and improper disposal will persist as an environmental aggravating factor since not all biobased polymers are biodegradable. Furthermore, biobased polymers are only classified as biodegradable and/or compostable under specific conditions as described in ASTM D6400, D5988-18, and ISO 14855 standards.^{1,8}

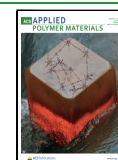
On the other hand, recycled materials with the necessary approvals can also be used to manufacture plastic packaging intended to come into contact with food, as described in many studies and indicated by the European Commission and other amendments.^{9–11} Moreover, if the packaging is intended to

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contact food, it must not pose any risk to consumers of ingesting hazardous substances transferred from the packaging to food.^{12–14}

Although it may seem contradictory initially, several studies have investigated the recycling of biobased polymers, specifically those made of PLA, due to their good recyclability and biocompatibility properties.^{15–19} In addition, using recycled biobased polymers can improve the added value of the material since their production from renewable sources is frequently more expensive than petroleum-based counterparts.

One of the concerns about adopting the conventional recycling process applied to postconsumer materials from nonrenewable sources, such as poly(ethylene terephthalate) (PET) and polypropylene (PP), to biobased polymers, is the washing stage, which uses high temperatures and alkaline solutions that can catalyze the degradation process by basic hydrolysis, affecting the material's physicochemical properties and making it impossible to recycle. However, some studies focusing on optimizing the washing parameters for recycling PLA have shown that reducing the molar mass can be controlled.^{20,21} Paiva et al. demonstrated in an in-depth study of these variables that using experimental design can reduce the impact on molar mass during the washing process while maintaining the properties of the biobased polymer.²⁰

Thus, this work has important relevance to the study of PLA biobased polymer recycling, analyzing the stages of the recycling cycle, which are (i) postconsumer packaging material using the contamination protocol proposed by the FDA, (ii) washing process, and (iii) mechanical recycling. This approach is particularly valuable as it not only addresses a significant gap in the current literature—where a fully detailed recycling cycle for biobased polymers, particularly for food contact applications, remains unexplored—but also offers practical insights directly applicable in industrial settings, especially concerning the mitigation of contaminants. By detailing each stage, this study contributes to optimizing recycling processes, reducing environmental impact, and promoting the sustainable management of biobased polymer waste.

Understanding the migration of contaminants is crucial to ensuring the safety of recycled products, especially for applications involving food contact. Monitoring and understanding the behavior of migration of these substances allow for the development of more accurate standards and regulations. Furthermore, establishing theoretical aspects to predict and understand migration behavior enables anticipating potential risks and optimizing recycling processes and polymer formulations, thereby advancing material science and creating safer, more efficient solutions for biobased polymers.

In this sense, the efficiency of recycling in decontaminating these materials was evaluated through migration tests in different simulants and the total dissolution of the pellets after the process. The contaminants were analyzed using solid-phase microextraction employed direct injection into the gas chromatograph coupled to a mass spectrometer using the DI–SPME–GC–MS technique. The understanding of these behaviors was only elucidated through an in-depth evaluation of Hansen's solubility parameter and a theoretical methodology capable of evaluating the molecular volume of each system, as well as the interaction energy between each contaminant and the monomeric structure of PLA.

2. MATERIALS AND METHODS

2.1. Chemicals. The chemicals used for the FDA contamination protocol were benzophenone (Across Organics, 99%, CAS 119-61-9), tetracosane (Merck, 99%, CAS 646-31-1), toluene (Vetec, 99.5%, CAS 108-88-3), heptane (Synth, 99%, CAS 142-82-5) and chloroform (Vetec, 99.8%, CAS 67-66-3). Sodium hydroxide (Panreac, 98% CAS 1310-73-2) and Triton X-100 (Exôdo Science, CAS No. 9036-19-5) were used for washing. For the dissolution protocol, ethanol (EtOH) (No. CAS 64-27-5), and dichloromethane (DCM) (No. CAS 75-09-2) were purchased from Panreac (Barcelona, Spain).

Ethanol (HPLC grade No. CAS 64-27-5) and acetic acid (Sigma-Aldrich, 99.8%, CAS No. 540-84-1) were supplied by Scharlau Chemie S.A. (Sentmenat, Spain) and used to prepare food simulants. Ultrapure water was obtained from a Milli-Q Ultrametric Wasserlab GR 216071 (Barbatina, Spain).

2.2. Samples. The commercial biobased polymer used in this work was poly(lactic acid), PLA Ingeo 4043D, with an L-lactide content of 98%, supplied by NatureWorks. The polymer had a melt flow index (MFI) of 6 g/10 min (ASTM D 1238), 210 °C, and 2.16 g/cm³ (ASTM D792). A challenge test was applied to demonstrate the efficiency of the decontamination technology under study.

2.3. Sample Preparation. **2.3.1. FDA Contamination Protocol of Poly(lactic acid) Pellets.** The PLA pellets were subjected to a forced contamination protocol procedure (challenge test) described in the USFDA (2006).²² The protocol is described as a contamination cocktail containing a mixture of surrogates representing the worst postconsumer conditions to which a plastic package can be subjected. As described previously, these contaminants encompass a diverse range of chemical substances that could potentially expose consumers to harmful compounds. The concentrations used in this study were deliberately elevated to simulate a worst-case scenario. The surrogate cocktail comprised chloroform, toluene, tetracosane, and benzophenone.²² Chloroform and toluene were selected as they are standard components of cleaning solvents, benzophenone was chosen to represent nonvolatile polar pesticides, and tetracosane was included to simulate motor oil contamination. Although this protocol is widely used for polymers such as PET and PP, it can also be applied to all recyclable polymers that will be employed in food-contact material, including PLA-simulating plastic packaging with high recycling potential.^{22–26}

In the first step, PLA was immersed in the contamination cocktail for 14 days in a hermetically sealed chamber under constant agitation at a controlled temperature of 40 °C. The surrogates used in the cocktail have physicochemical characteristics that cover a wide class of possible contaminants that can be present in postconsumer packaging. The physicochemical characteristics of the compounds used in this step and their concentrations, as determined by the FDA protocol, are listed in Table 1.

Table 1. Concentration and Properties of FDA Protocolled Contaminants (Surrogates) Used in a Cocktail

contaminants	concentration	properties
benzophenone	1% (m/v)	non-volatile polar
tetracosane	1% (m/v)	non-volatile and non-polar
heptane	78% (v/v)	volatile and non-polar
chloroform	10% (v/v)	volatile polar
toluene	10% (v/v)	volatile non-polar

Afterward, PLA pellets were subjected to washing and mechanical recycling, as described below.

2.3.2. Washing and Mechanical Recycling. As described earlier, the washing process is similar to that used in the plastics recycling industry for plastics made from conventional nonrenewable source polymers. In this way, the parameters used in the washing process were the same as those studied by Paiva et al.²⁰ To minimize the effects of degradation by hydrolysis that PLA can suffer, the following washing conditions were used: sodium hydroxide 2% (w/w) and

surfactant 3% (w/w) as the washing solution, applied for 15 min at 75 °C.

Mechanical recycling of PLA was performed using a Thermo Scientific Process 11 Parallel Twin-Screw Extruder with a 40 L/D barrel length, 11 mm diameter screw, and standard configuration using push screws. The samples went through four recycling cycles at 200 °C, using the corotation speed of 400 rpm and feed rate of 3% during the extruder. Table 2 describes the samples and terminology used in this work.

Table 2. Description of the PLA Samples for Migration and Dissolution Testing

sample	nomenclature	description
1	PLAc	PLA contaminated
2	PLAcw	PLA contaminated and washed
3	PLAcR	PLA contaminated and mechanically recycled
4	PLAcwr	PLA contaminated, washed, and recycled

2.3.3. Total Dissolution Methodology. This methodology was developed and applied by Ubeda et al.²⁷ This protocol was adequate for the determination and quantification of volatile compounds in biobased polymers. In this protocol, 0.25 g of PLA pellets stored in 20 mL glass vials were dissolved in 3 mL dichloromethane solvent in an ultrasonic bath for 1 h. Then, 6 mL of ethanol was added to the solution, acting as an antisolvent, and the mixture was centrifuged at 500 rpm for 15 min. The supernatant was removed, and the mixture was filtered through a 0.25 μm PET filter. Triplicates of each sample were prepared, and the compounds were injected into a gas chromatograph coupled to a mass spectrometer (GC–MS) by liquid injection (LI) and solid-phase microextraction (SPME). Aznar et al. systematically studied this methodology to determine nonvolatile components based on polyester and PLA in biodegradable food packaging. Its effectiveness in dissolving samples and not detecting the apparent reabsorption of the analyte after reprecipitation was demonstrated.²⁸

2.4. Migration Tests. The PLA samples were subjected to a migration test in order to determine the transfer of surrogates from packaging to food simulants at different recycling steps. The simulants used for the study were simulant C, ethanol 10% (v/v), and simulant

B, acetic acid 3% (v/v). Both simulants are assigned to food with a hydrophilic character. Food simulant B shall be used for those foods with a pH below 4.5.⁹ Furthermore, migration tests were performed by total immersion. For this purpose, 2 cm × 3 cm pieces of the samples were placed in 20 mL vials, and 20 g of the simulant was added according to the rate of 6 dm² contact surface/kg of simulant, established by Regulation EU/10/2011. Once the vials were filled with the simulant, they were subjected to the following migration conditions: 10 days at 40 °C and 10 days at 60 °C. Both test conditions are established in the legislation to simulate storage at room temperature and mild conditions so as to not compromise the integrity of the PLA.⁹

2.5. Analysis by GC–MS. As described previously, the contamination cocktail contained volatile and semivolatile compounds, and for better performance in the analysis of these compounds, both SPME and liquid injection were tested. In the case of total dissolution samples, chloroform, and heptane were analyzed by SPME, and toluene, benzophenone, and tetracosane were analyzed by direct liquid injection (1 μL) since they provided better sensitivity. Migration samples were all analyzed by SPME. For the analysis of the total dissolution samples, 20 μL of the extracts were added to a 20 mL vial that was hermetically closed and analyzed by headspace SPME (HS-SPME). For the analysis of migration samples, 15 mL of the migration solutions were transferred to the vials that were hermetically closed and analyzed by total immersion SPME (TI-SPME). The SPME fiber used for the analysis was a DVB/CAR/PMDS 50/30 μm. This fiber was selected based on its microporous structure, which has been reported in the literature^{29,30} to increase extraction efficiency. The SPME extraction temperature and time conditions were 60 °C and 15 min, respectively.

GC–MS analysis was performed in a CTC Analytics CombiPal instrument from CTC Analytics AG (Zwingen, Switzerland) coupled to a GC 6890N gas chromatograph from Agilent (Palo Alto, CA, USA). The separation of the analytes was performed on an Agilent HP-5 MS column (30 cm × 0.25 mm, 0.25 μm layer thickness). The temperature program used started at 40 °C for 5 min and increased by 10 °C min⁻¹ to 300 °C hold for 1 min. The injector temperature was 250 °C, and helium was used as the carrier gas at a flow rate of 1 mL min⁻¹. An Agilent 5975 mass spectrometer was used as the MS source, and a quadrupole temperature detector was set at 230 and 250 °C, respectively. The SIM mode was used for acquisition with the

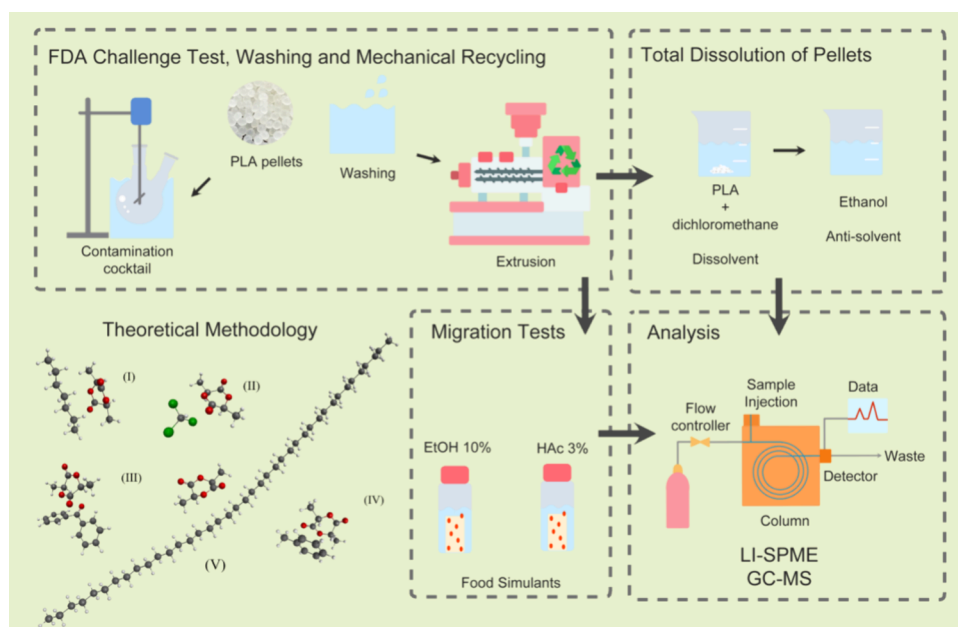


Figure 1. Flowcharts of the work: FDA challenge test, washing and mechanical recycling steps, total dissolution of pellets, migration tests, analysis, and theoretical methodology.

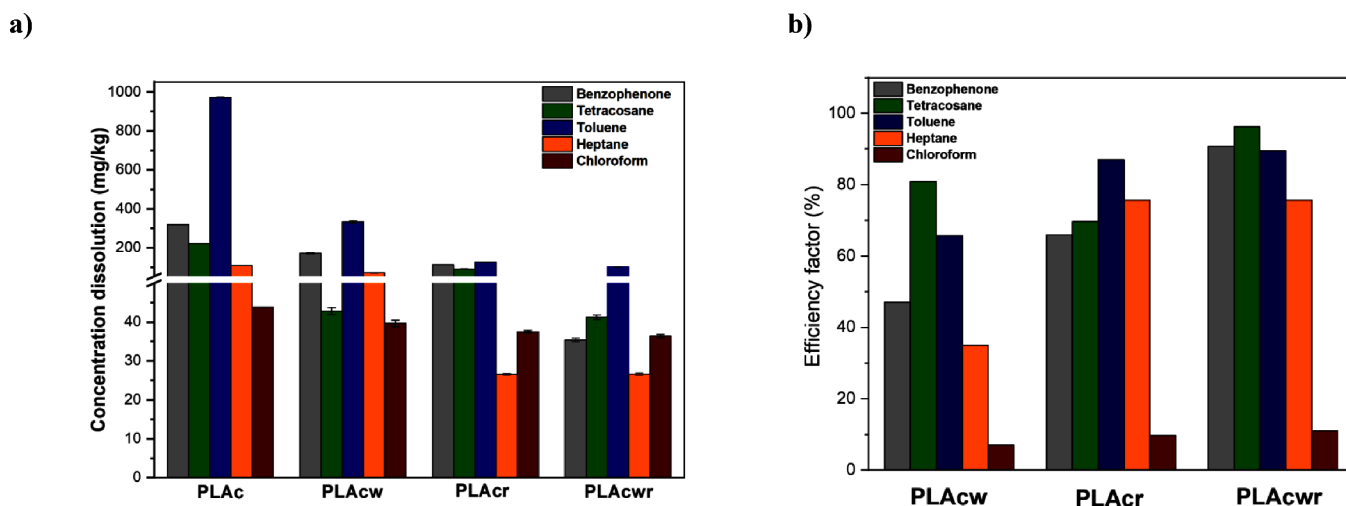


Figure 2. (a) Contaminants concentration for the samples and (b) efficiency factor for PLA decontamination.

following ion parameters: chloroform (83.00 and 118.00 m/z), heptane (57.00 and 71.00 m/z), toluene (51.00 and 91.00 m/z), benzophenone (77.00 and 105.00 m/z), and tetracosane (338.00 m/z).

Standard solutions were prepared in DCM:EtOH (1:2) (similar to the final solvent of the PLA dissolution protocol) and in both food simulants (EtOH 10% and HAC 3%) for quantitative analysis. The analytical parameters of the methods used were determined: linearity, linear range, limits of detection (LOD), and limits of quantification (LOQ). LOD and LOQ were determined by applying SPME–GC–MS to pure standards of the compounds under the same analytical conditions as those applied.

2.6. Theoretical Methodology. Electronic structure calculations theoretical computational methods and the solubility model proposed by Hansen were used to discuss the polymer–solvent/nonsolvent interaction.^{31,32} The structure of each system, heptane, chloroform, benzophenone, toluene, tetracosane, and PLA monomer was optimized at the GFN2-XTB method,³³ as implemented in the ORCA program.³⁴ The L-lactic molecule was considered for modeling the PLA system because electronic structure calculations using the actual polymer would be impractical. Furthermore, at the atomic level, these calculations allow us to rationalize the main local interactions present in the macroscopic system. All structures were confirmed as a minimum in the explored potential energy surface. The GEPOL algorithm, though the solvation model based on density (SMD) at the DFT/M06-2X/def2-TZVP level of theory,^{35,36} was used to evaluate the molecular volume of each system in the heptane solvent. Furthermore, the interaction energy (ΔE), based on the GFN2-XTB energies, between each contaminant and the PLA monomer was estimated by considering the cluster (PLA + contaminant) with the lowest energy. The noncovalently bound complexes (PLA + contaminant) with the lowest energy were found using the NCI model CREST program.³⁷ Finally, Figure 1 shows the flowcharts of the work from the PLA recycling steps to sample preparation and subsequent chromatographic and theoretical-computational analysis.

3. RESULTS AND DISCUSSION

3.1. Influence of the PLA Recycling Cycle on the Concentration of Contaminants. **3.1.1. Contaminants Teor on Pellets: Experimental and Theoretical Approach.** Figure 2a shows the concentration of contaminants in the PLA pellets, which is the initial concentration of surrogates. The actual concentration of contaminants present in PLA was analyzed for the contaminated samples before and after the recycling cycle, being analyzed at each cycle stage. Furthermore, Figure 2b shows the results of calculating the

Efficiency factor of the recycling process in decontaminating the samples by eq 1, comparing each stage of the recycling cycle to the complete process. In addition, the analytical parameters of the FDA contaminant protocol calibration curves are provided in the Supporting Information (Tables S1 and S2). Furthermore, Table S3 (Supporting Information) shows the same results of the concentration of surrogates that migrated to the two different simulants under different migration conditions for a better interpretation of the data.

$$E_f(\%) = \frac{C_i - C_f}{C_i} \quad (1)$$

where C_i is the initial concentration of the contaminants present in the PLA sample, PLAc, and C_f is the final concentration after the recycling steps.

After the washing stage was completed, there was a significant decrease in the concentration of the contaminant tetracosane, plummeting from 223.30 to 46.84 mg/kg. In contrast, samples solely subjected to the mechanical recycling stage showed a lesser reduction (91.12 mg/kg), showing that this step is fundamental. However, a reverse trend emerged when heptane was analyzed in the same samples. The mechanical recycling stage proved to be more effective in reducing heptane concentration, registering 26.53 mg/kg compared to 71.08 mg/kg for the washing stage, despite the initial concentration of 109.38 mg/kg for PLAc.

As can be seen in Figure 2b, individually, the washing (PLAcw) and mechanical recycling (PLAcR) steps have shown high efficiency in reducing the concentration of contaminants, with the mechanical recycling step being more effective than the washing step values above 60%. However, the combination of the two steps (PLAcwr) is more effective than each individual step because, as described above, the decontamination efficiency for some surrogates is more significant in one step than in the other. In general, when comparing final values with the high levels of contamination before the process, it can be seen that the recycling cycle showed great potential in the decontamination process.

The content of contaminants present in a polymer sample after contact with the cocktail to simulate the worst case depends on thermodynamic factors. This complexity can be understood in the same way as the solubility of polymers since migration into polymers depends on phases similar to those of

solubilization. In both processes, first, the solvent needs to wet the polymer. Then, the solvent and contaminants diffuse into the polymer, causing it to swell. This process may take several hours or longer for polymers of high molar mass depending on sample size, temperature, and other factors. Thus, our discussion will focus on (1) solubility parameter aspects, which guide the initial phase and entry of contaminants into the polymer, (2) molecular volume, which directly impacts diffusivity into the polymer, and (3) vapor pressure, discussed through interactions and in a liquid–vapor equilibrium, and its permanence in the liquid medium to allow contamination of the polymer.

Considering that the first step is associated with the interaction between polymer and contaminants, a model used to evaluate the solubility/interaction between a polymer and a solvent or nonsolvent was proposed by Hansen.^{31,32} This theoretical-experimental model defines solubility in terms of the cohesive energy density of the molecule (δ_H), which can be described from the partial contributions of three main intermolecular interactions described in Hansen's extended equation (eq 2).³¹

$$\delta_H = \sqrt{\delta_d + \delta_p + \delta_h} \quad (2)$$

where δ_d is the dispersive interaction, δ_p is the polar interaction and δ_h is the hydrogen bonding interaction. These components are listed for the PLA and for each of the compounds present in the cocktail, Table 3. For PLA the components are listed in

Table 3. Hildebrand Solubility Parameters, Vapor Pressure, and Theoretical Molecular Volume of the Compounds Present in the Contamination Cocktail^a

compound	δ_d ^{0.5} (MPa) ^{0.5}	δ_p ^{0.5} (MPa) ^{0.5}	δ_h ^{0.5} (MPa) ^{0.5}	P^0 (hPa)	molecular volume (Å ³)
PLA	18.6	6.0	9.9		194.3
benzophenone	19.6	8.6	5.7	1.33	211.7
chloroform	17.8	3.1	5.7	210	140.9
toluene	18.0	1.4	2.0	30.88	109.6
heptane	15.3	0	0	111	136.5
tetracosane					707.9

^a δ_d = dispersive interaction; δ_p = polar interaction; δ_h = hydrogen bonding interaction, and P^0 = vapour pressure.

Table 3 and its solubility ratio is $R_0 = 8$.³¹ In addition, Table 3 presents the molecular volume of each system obtained at the SMD (heptane)-DFT/M06-2X/def2-TZVP level of theory, as described above. It has been hypothesized that analyzing these parameters allows associating a higher content of migrants since chemical affinity is the first thermodynamic barrier to be overcome and will dictate the amount of diffusion into the polymer. In addition, the molecular volume associated with thermodynamic factors may affect the process of diffusion of contaminants into the polymer.

In addition, eq 2 and the tabulated components allow us to quantify the polymer's solubility from the interaction distance, D , as described in eq 3.

$$D = \sqrt{4(\delta_{dsol} - \delta_{dpol})^2 + (\delta_{psol} - \delta_{ppol})^2 + (\delta_{hsol} - \delta_{hpol})^2} \quad (3)$$

Finally, from eq 3 and the solubility radius of PLA, a three-dimensional solubility sphere can be represented in Figure

3a.³¹ The solubility sphere makes it possible to analyze the polymer–solvent/nonsolvent interaction since the smaller this interaction distance, the greater the potential for the compound to be classified as a good solvent, which means that it has a higher interaction with the polymer. It has been hypothesized that analyzing these parameters allows associating a higher content of migrants since chemical affinity is the first thermodynamic barrier to be overcome and will dictate the amount of migrants diffused into the polymer.

A rudimentary examination of Figure 3a enables us to deduce that chloroform and benzophenone exhibit favorable solvent properties, whereas toluene and heptane can be categorized as nonsolvents. Nevertheless, upon conducting a comparative analysis with Figure 2 for the PLAc sample, it becomes apparent that greater diffusivity into PLA was observed with the contaminants toluene, benzophenone, tetracosane, heptane, and chloroform in sequential order. However, the model has its limitations, and as noted, it was not possible to analyze the polymer–solvent/nonsolvent interaction for tetracosane because the Hildebrand solubility parameters for this compound are not available in the literature.

Another way to discuss the interaction between the PLA monomer and each compound in the cocktail contamination is to calculate the electronic structure to obtain the interaction energy, ΔE (eq 4), allowing comparisons on a perfectly equal footing.

$$\Delta E = E_{\text{cluster}} - (E_{\text{PLA}} + E_{\text{contaminant}}) \quad (4)$$

where E_{cluster} is the energy of the lowest energy cluster formed between the PLA monomer and a molecule contaminant (Figure 3b), E_{pla} is the energy of the PLA monomer, and $E_{\text{contaminant}}$ is the energy of a molecule contaminant. The ΔE for each system is shown in Table 4.

As can be observed, the system with the highest interaction energy is benzophenone/PLA, foremost due to its polar affinity, while the heptane/PLA system shows the lowest interaction energy. Therefore, estimated ΔE values based on electronic structure calculations can be an interesting tool to predict and analyze the overall interaction trend between contaminating molecules and polymers. Specifically, in this study, there is an agreement between the data obtained by the Hansen sphere and the theoretical methodology, both presented in Figure 3. The only exception is chloroform, whose behavior may be partially attributed to its vapor pressure at the experiment's temperature. During the contamination process, which followed the FDA protocol, the PLA was immersed in a cocktail for 14 days at 40 °C in a closed system. However, under these conditions, contaminants with higher vapor pressures could vaporize during the contamination and also during the sample preparation and recycling steps. As a result, the presence of these contaminants depends on their volatility, meaning that those with higher vapor pressures are less readily available in the immersion process.

The Hansen interaction model, based on solubility parameters, is an effective tool for predicting the affinity between contaminants and PLA, considering dispersion, dipole, and hydrogen bonding interactions. This model allows for a precise estimation of the affinity between contaminants and the polymer, aiding in the prediction of contaminant content. Applying an additional mathematical model complements this analysis, providing detailed quantitative predictions

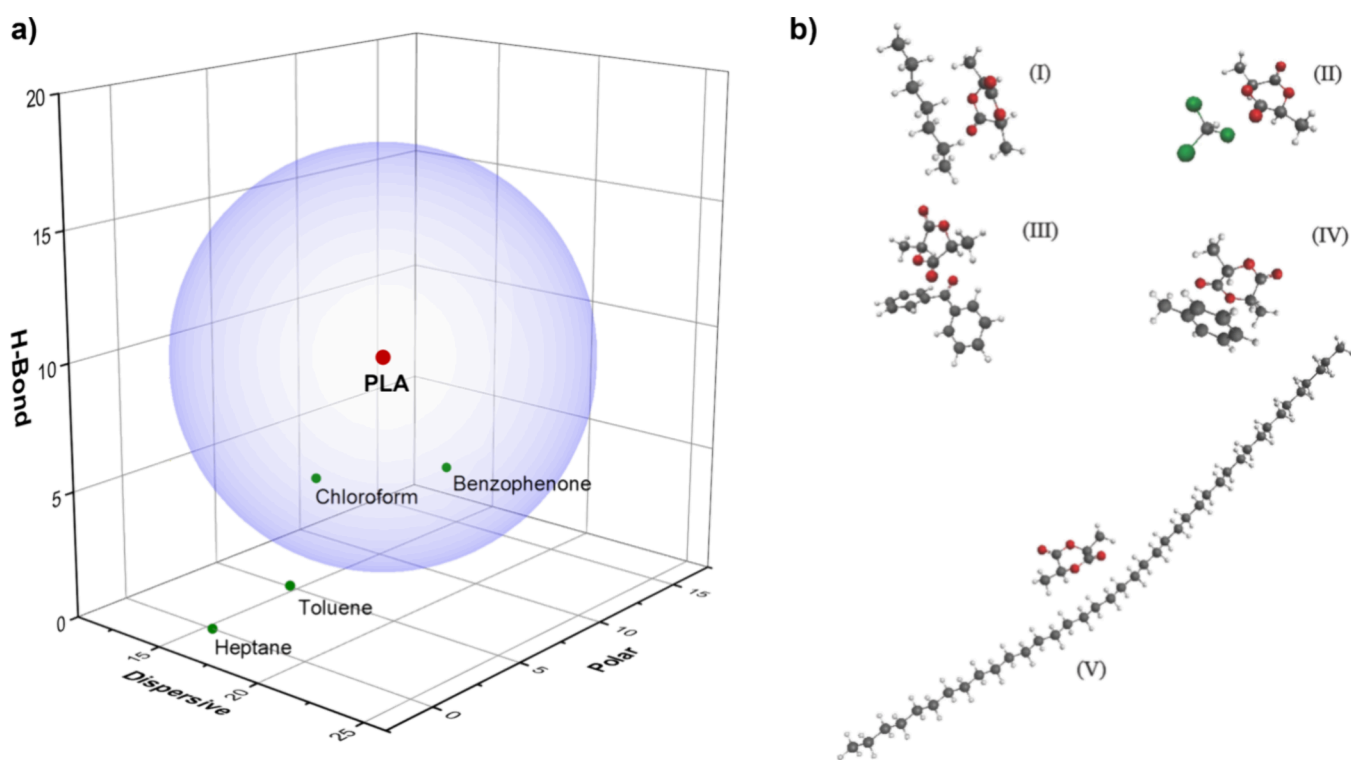


Figure 3. (a) Sphere of solubility of PLA and the solubility parameter components of contaminants, and (b) the lowest energy aggregates formed between PLA monomer and each molecular contaminants (I) heptane, (II) chloroform, (III) benzophenone, (IV) toluene, and (V) tetracosane. Hydrogen = white; oxygen = red; chlorine = green.

Table 4. Lowest Energy Interaction System

system ^a	ΔE (kJ mol ⁻¹)
heptane/PLA	-23.04
chloroform/PLA	-29.50
benzophenone/PLA	-53.12
toluene/PLA	-32.44
tetracosane/PLA	-24.83

^aIn ΔE calculations, the L-lactide unit was used to model the local structure of PLA.

of the interactions and behaviors of contaminants in PLA. An analysis of Figure 2a for the PLAc samples suggests that both models are effective tools for assessing contamination in these systems. The contaminants present in the highest concentrations are toluene and benzophenone, which exhibit the lowest interaction energies and, consequently, the strongest affinity with PLA. Although toluene is not within the solubility sphere, it is positioned close to it. In contrast, a different pattern is observed for heptane and tetracosane, which show the lowest values in Figure 2a, maintaining consistency with the predictions. As previously mentioned, various factors can influence contaminant uptake, and in the case of chloroform, chemical affinity does not appear to be the primary factor governing its migration behavior in PLA.

3.1.2. Effect of Recycling Processes on Migration Analysis in Various Food Simulants. After analyzing the total content of contaminants present in the PLA pellets through complete dissolution, the samples underwent a migration test using two different food simulants (3% acetic acid and 10% ethanol) under various migration conditions. Figure 4a,b show the results for the nonpolar contaminants (heptane and toluene),

while Figure 4c,d show the results for the polar ones (benzophenone and chloroform).

In this way, as observed in the dissolution results, for the nonpolar surrogates (Figure 4a,b), a drastic decrease in their concentration was observed when the biobased polymer was subjected to the total recycling cycle (PLAcwr), compared to the samples that went only through the washing process (PLAcw) or the mechanical recycling (PLAc). This behavior can be seen for all migration test conditions and food simulants. Furthermore, as described in the literature, the diffusion process is related to the molar mass, which means that the lower the molar mass of a compound, the higher its diffusion process.^{38,39} However, Paiva and co-workers reported that in the case of contaminant migration, this relationship is not limited, and other factors should be considered, mainly the physical and chemical characteristics of both the polymeric matrix and the food simulants, paying more attention to the triple interaction polymeric matrix-surrogates-food simulants. Furthermore, the entire recycling cycle still proved to be the most efficient process for decontaminating PLA.

On the other hand, when the concentration of polar contaminants was analyzed (Figure 4c,d), different aspects of the polymer matrix-surrogate interaction from those observed for the nonpolar contaminants were observed.

As mentioned above, PLA is a polar polymer with carbonyl and hydroxyl groups throughout its structure, which increases its interaction with polar compounds. In this way, an increase in concentration was observed for the benzophenone surrogate upon comparison of the contaminated sample (PLAc) with the samples that had undergone the recycling cycle. Comparing migration tests at 40 °C for HAc 3% and EtOH 10% simulants, there was a higher concentration of benzophenone in the alcoholic simulant due to the high polarity, making the

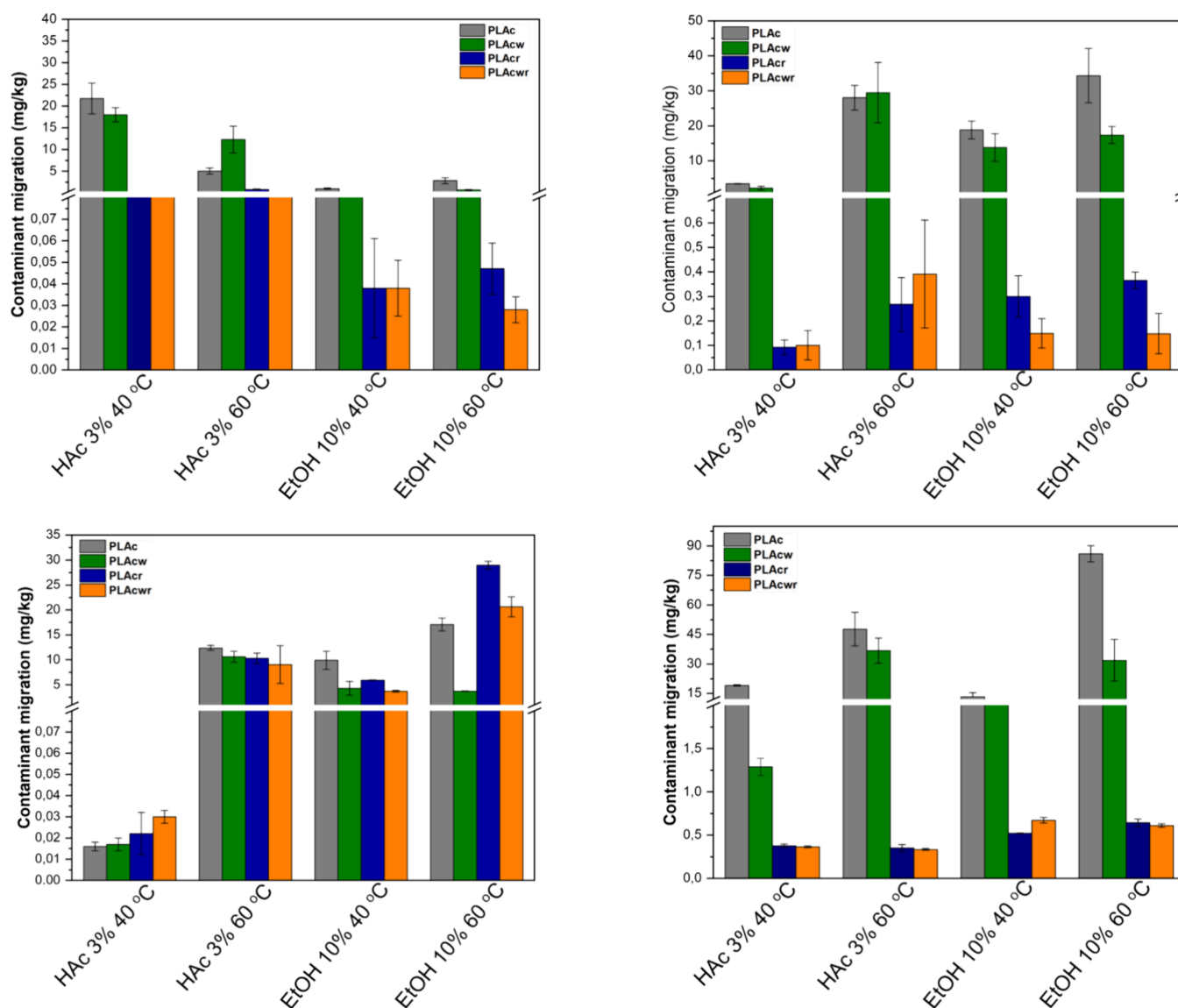


Figure 4. Comparison of concentration of contaminants in different migration tests for all PLA samples and analyzed by nonpolar (a,b) and polar (c,d) surrogates.

surrogate—simulant interaction greater. However, when the temperature of the tests was increased, there was an increase in concentration for both the acidic and alcoholic simulants, indicating that the polarity factor had no longer a high influence compared to temperature.

The polarity of the simulants and the temperature used for the migration tests may increase the diffusion of this contaminant since the temperature used in the test (60 °C) was higher than the glass transition, T_g , of PLA (~57 °C). In this condition, the mobility of the polymer chains of the amorphous phase facilitates the diffusion process.^{15,16} In fact, in the dissolution, the benzophenone followed the same pattern as the nonpolar compounds; all those concentrations decreased on the individual recycling steps (PLAcw and PLAcR) and the total cycle (PLAcwr). In addition, the dissolution process can result in the loss of analyte due to the extraction and reprecipitation steps, which can affect the actual concentration analyzed. For chloroform, the concentration of the samples that underwent the dissolution protocol remained close in value. Furthermore, the use of DCM solvent

interferes with the concentration due to the similarity between the solvent and the analyte analyzed.

On the other hand, the quantification and analysis of the recycling efficiency decontamination of tetracosane was only possible in the dissolution process, remaining always below the detection limit for the samples submitted to the migration tests. Tetracosane represents the class of nonpolar and nonvolatile contaminants with long chain and high molar mass, 338.65 g/mol, and therefore, its interaction with the polymer matrix is low, which justifies its concentration below the detection limit for the migration tests.

As outlined in European Regulation 10/2011, Article 11, substances with specific restrictions must not exceed their assigned specific migration limit (SML). For substances without an SML, the generic migration limit of 60 mg/kg applies. In this context, the contaminants used in the FDA's challenge test included only benzophenone, which has an SML of 0.6 mg/kg. As previously discussed, the concentration of cations increases throughout the recycling steps, exceeding the established limit. However, for the other contaminants, a

decrease in concentration is observed as the samples progress through the recycling stages, reaching levels below the limits set by the legislation. Moreover, this trend is consistent across both simulants and under both migration test conditions, demonstrating the effectiveness of recycling in reducing contamination levels.

One of the concerns pointed out in some studies is the migration of intentionally and nonintentionally added substances (IAS and NIAS) during the migration tests, especially the NIAS formed by the degradation of PLA. Ubeda et al.⁴⁰ identified the migration of monomer dimethyl-1,4-dioxane-2,5-dione (lactide), derived from lactic acid dimer, which is not on the positive list of European Regulations.⁴¹ For these substances, the concentration must be controlled and follow the recommendation of the European Commission (<0.01 mg/kg). However, in this study, the presence of this monomer was not a factor that affected the experimental results since the target mode analysis and system parametrization efficiently determined only the compounds present in the contamination cocktail in the FDA challenge test.

4. CONCLUSIONS

In this study, the recycling process applied to previously contaminated PLA pellets was evaluated with regard to the presence of contaminants, as well as their migration and interaction with PLA. A comparative analysis of contaminant concentrations in PLA pellets and those migrating to various food simulants was conducted, revealing the remarkable effectiveness of the recycling process in reducing contaminants, with concentrations in PLA pellets exceeding 40 mg/kg and reaching up to 800 mg/kg for certain surrogates. The research also delves into the nuanced interactions between different contaminants (both polar and nonpolar) and the biopolymer at different stages of the recycling process, revealing a complex interplay influenced by factors such as molar mass, physical and chemical properties, and the specific conditions of migration tests. In addition, the study provides critical insight into the impact of recycling on the structural integrity of PLA, with microscopic images revealing changes in the surface structure after recycling and migration testing. The results presented for both the dissolution and migration tests prove that each stage of the recycling cycle is important in the decontamination process. The individualized assessment of each contaminant under different conditions provided a broad overview of the contaminants' input and output. Furthermore, the dissolution protocol and the migration tests for different simulants were complementary techniques that increased reliability and explored in different ways the characteristics of both the polymer matrix-surrogate-simulant interaction and the diffusion processes related to the physicochemical properties of the material and the contaminant. Moreover, the FDA contamination protocol, originally developed for conventional polymers, was found to be applicable to biopolymers, such as PLA, demonstrating a high degree of interaction between the contaminant cocktail and the biopolymer. This applicability ensures that worst-case post-consumer conditions of a package can be effectively analyzed, providing a robust framework for evaluating contamination and decontamination in biopolymers. The migration of contaminants is influenced by the theoretical molecular volume of the contaminants, the type of food simulant, the test temperature, and the interactions between polymers and surrogates. Interaction energy values estimated from electronic

structure calculations are a valuable tool for predicting and analyzing the overall trends in interactions between contaminant molecules and polymers. Remarkably, there is strong consistency between the results obtained from the Hansen sphere analysis and those derived from the theoretical approach.

The recycling of biobased polymers to return this product to its original application is in line with aspects of sustainability, and in this sense, the results presented shed light on the theme of food safety based on the quantification of contaminants supported by quantum chemical calculations.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsapm.4c02230>.

Details on analytical calibration and migrant analyte concentration results (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Sandra A. Cruz – Chemistry Department, Center for Exact Sciences, Federal University of São Carlos (UFSCar), SP-310 São Carlos, Brazil; orcid.org/0000-0002-5548-0166; Email: sandra.cruz@ufscar.br

Authors

Robert Paiva – Chemistry Department, Center for Exact Sciences, Federal University of São Carlos (UFSCar), SP-310 São Carlos, Brazil; Department of Analytical Chemistry, Aragon Institute of Engineering Research I3A, CPS-University of Zaragoza, 50018 Zaragoza, Spain

Margarita Aznar – Department of Analytical Chemistry, Aragon Institute of Engineering Research I3A, CPS-University of Zaragoza, 50018 Zaragoza, Spain

Magdalena Wrona – Department of Analytical Chemistry, Aragon Institute of Engineering Research I3A, CPS-University of Zaragoza, 50018 Zaragoza, Spain; orcid.org/0000-0003-2052-3012

Ana Paula de Lima Batista – Chemistry Department, Center for Exact Sciences, Federal University of São Carlos (UFSCar), SP-310 São Carlos, Brazil; orcid.org/0000-0002-9675-6106

Cristina Nerín – Department of Analytical Chemistry, Aragon Institute of Engineering Research I3A, CPS-University of Zaragoza, 50018 Zaragoza, Spain; orcid.org/0000-0003-2685-5739

Complete contact information is available at: <https://pubs.acs.org/10.1021/acsapm.4c02230>

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