Design of Experiments as a tool for post-consumer PLA packaging recycling: correlation between washing parameters and degradation

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Research Article

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Abstract

The increasing demand for sustainable packaging solutions has led to the widespread adoption of biodegradable polymers such as polylactic acid (PLA) in the packaging industry. However, the efficient recycling of post-consumer PLA packaging remains a challenge due to contamination from residual food and other substances. This study presents the application of Design of Experiments (DoE) in the evaluation of washing parameters, typically used in the recycling industry, in the degradation of post-consumer biodegradable PLA packaging. A series of experiments were conducted using a factorial design to investigate the effect of key washing parameters, including NaOH concentration, washing temperature, washing time, and surfactant concentration, on the degradation of PLA. The degradation was accompanied by rheology employing the Cox-Merz rule, which establishes the relationship between complex viscosity and steady state viscosity. The results indicated that a washing process with lower degradation rates could be obtained by adjusting the washing parameters within specific ranges. The application of DoE allowed the identification of the most influential factors and their interactions in the degradation of PLA during the washing step. This study demonstrates that this is a valuable tool in the development of sustainable recycling processes for biodegradable packaging materials, contributing to a circular economy and reducing environmental impact.

1. Introduction

The use of biodegradable polymers, either from non-renewable or renewable sources, in the production of packaging for food contact and hospital products is one of the most discussed topics in the world today. The concern is related, besides other aspects, to the environmental problem caused by the inadequate disposal of non-biodegradable post-consumer plastic materials [1, 2]. Moreover, with the advent of the pandemic caused by the COVID-19 virus, there has been an exponential increase in the use of quick disposal materials produced from conventional polymers, which has directly impacted the environment and especially marine life [3, 4].

One of the proposals to be implemented in the new EU directives is the total elimination of the use of pristine petroleum polymers in single-use manufacturing. The directive aims to encourage the use of recycled and/or biodegradable polymers from renewable sources to mitigate environmental impact [4, 5].

In fact, the new proposals can positively affect the circular economy and reduce the environmental impact caused by these materials [5]. In addition to the cost of producing plastic packaging from biodegradable polymers, another problem remains: the mishandling of post-consumer packaging. Although it is biodegradable and comes from a renewable source, biodegradation only occurs under specific conditions as described in ASTM-D-883 [6].

Poly (lactic acid), PLA, is one of the most widely used biodegradable biopolymer from renewable sources in the plastic packaging, pharmaceutical industries, and in the production of rapidly disposable hospital products. This fact is due to its biocompatibility, availability of commercialization on large scale, and
wide range of grades, which allows it to be used in the same manufacturing processes as conventional thermoplastic resins, such as extrusion, molding, lamination, and other [7]. Data from 2020 indicate that PLA represented more than 10% of the global production and commercialization of the bioplastics market, making it a promising candidate to meet the new directives established by regulatory agencies [7].

As mentioned earlier, the European directives aim to encourage the use of recycled packaging for direct or indirect contact with food. In this way, an alternative that has been studied is the recycling of post-consumer biodegradable packaging by means of pre-established procedures for packaging made of conventional polymers such as polyethylene terephthalate (PET), polypropylene (PP) and other thermoplastic resins [8, 9]. However, some reasons are taken into consideration to propose the recycling of biodegradable plastics (i) the increasing industrial demand, due to development and population growth (ii) the reduction of the consumption of non-renewable resources, (iii) cost of the biopolymer production, (ix) some compostable materials do not suffer total degradation, what can cause the residual accumulation and the loss of the raw material that could be reused [10–13].

Therefore, several studies have investigated the possibilities of recycling biopolymers, with particular attention to PLA [10–12, 14–17]. It is known that this polymer thermodegrade during processing, and consequently its recyclability is strictly related to the actual extent of thermodegradation phenomena during the recycling stages [16, 18]. Amorin et al.[15] and Zhao et al. [19] subjected PLA to multiple reprocessing cycles and evaluated its impacts on the molar mass of the polymer. The results indicated that the increase in the number of cycles results in a reduction of the molar mass which directly affects the material properties. However, in the first cycles, the reduction and change in properties were minimal, indicating the feasibility of recycling.

Before the plastic material goes through the extrusion process, it first goes to a washing stage. This step is a process of extreme importance in recycling because it is at this stage that occurs the pre-decontamination of post-consumer plastic material. However, one of the problems presented in the recycling process of biodegradable polymers is their ability to suffer degradation by hydrolysis [20]. In this sense, the washing step becomes critical, since basic solutions and high temperatures are commonly used in the processes that can accelerate the degradation by hydrolysis. Despite its importance, no studies were found in the literature that systematically studies the variables washing process that influences the degradation of PLA. On the other hand, there are several studies in the literature on this theme applied to conventional polymers such as PET [21–24].

Therefore, this is a pioneering study that unites two themes at the forefront of knowledge: (1) biopolymer recycling and (2) the effect of washing variables on PLA degradation. Thus, to minimize the effects caused by the degradation by basic hydrolysis, and to maintain the primordial steps employed in the recycling industries, this study has as its goal the use of a Design of Experiment (DoE) to study the variables employed in the PLA washing process, which are sodium hydroxide (NaOH) concentration, washing temperature, washing time and the presence of surfactant and, having, as a result, a molar mass
index that can predict the ideal conditions to minimize the degradation process and maintain the properties of the material.

2. Material and Methods

2.1. Chemicals

The reagents used in this study were sodium hydroxide (Panreac 98%, CAS No. 1310-73-2), surfactant Triton X-100 (Exodo science, CAS No. 9036-19-5), and distilled water.

2.2. Samples

The commercial polymer used was poly(lactic acid), PLA Ingeo 4043D, from NatureWorks. The polymer presents a melt flow index (MFI) of 6 g/10 min (ASTM D 1238, 210 °C, 2.16 kg) and a density of 1.24 g/cm³ (ASTM D 792).

2.3. Washing process

To analyze the influence of the washing parameters a Design Experiment was employed to study these variables and relate them to the increase in the PLA degradation process. After the washing process, the PLA pellets were dried in a vacuum oven for 4 hours at 80 °C with subsequent analysis of their molar mass by rheometer.

2.4. Design of experiments

As described earlier, different variables were chosen based on the washing processes employed for PET and PP.

- (v1) NaOH concentration (%);
- (v2) washing temperature (°C);
- (v3) washing time (min);
- (v4) surfactant concentration (%).

The DoE results allow investigating of the influence of the combined variables from two levels, 1 (high) and -1 (low), as described in Table 1. Therefore, a full factorial design $2^4$ (Experiments 1 to 16) was obtained from the combination of the four variables in their two coded levels. The response analysed was the molar mass variation. Thus, a full of 19 experiments were developed, with three experiments being central point (CP). Moreover, for the analysis and organization of the data the Excel program was used, and to analyse the experimental parameters the ANOVA was applied to the proposed methodology.
Table 1

<table>
<thead>
<tr>
<th>Level coded</th>
<th>(v1)</th>
<th>(v2)</th>
<th>(v3)</th>
<th>(v4)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[NaOH] %</td>
<td>T °C</td>
<td>Time (min)</td>
<td>[Surfactant] %</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>75</td>
<td>15</td>
<td>3</td>
</tr>
<tr>
<td>-1</td>
<td>1</td>
<td>25</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>Central point</td>
<td>1.5</td>
<td>50</td>
<td>10</td>
<td>1.5</td>
</tr>
</tbody>
</table>

2.5. Determination of molar mass index

A parallel plate rheometer (Anton Paar- MCR501) was used to measure the complex viscosity ($\eta$) as a function of frequency ($\omega$). For the test, plates with a diameter of 25 mm were used at a temperature of 200 °C in a dynamic regimen and the range of frequencies used was 0.01 to 500 rad s$^{-1}$ at 1% as well as the gap between plates was 1.00 mm. The same methodology was employed by Garcia et al. [25]

The zero shear-rate viscosity, determined by rheometry, is associated with molar mass according to the Mark-Houwink equation (Eq. 1).

$$\eta_0 = KM^a \quad (1)$$

where M is the molar mass and K and $a$ are constants of the polymer[25].

When frequency sweep measurements are performed the Cox-Merz rule is usually used and establishes the relation between the complex viscosity ($\eta(\omega)$) with the steady state viscosity ($\eta(\dot{\gamma})$), represented by Eq. (2)[26].

$$\eta(\dot{\gamma}) = |\eta(\omega)| \text{; with } \dot{\gamma} = \omega \quad (2)$$

Through Equations 1 and 2, it is possible to calculate the ratio between molar masses $M_1/M_2$, where $M_1$ is the molar mass of analysed samples, $M_2$ is the molar mass of pristine PLA and $a$ is 3.4.

$$\frac{\eta_{01}}{\eta_{02}} = \frac{KM_1^a}{KM_2^a} \quad (3)$$

Furthermore, the ratio of the molar mass of the PLA samples can be calculated through Eq. (4).

$$\frac{M_1}{M_2} = \sqrt[100]{\frac{\eta_{01}}{\eta_{02}}} \quad (4)$$
when the $\eta_{01}$ and the $\eta_{02}$ represent the zero shear-rate viscosity of the samples and pristine PLA, respectively.

Thus, from Eq. (4) it is possible to quantitatively evaluate the molar mass variation of the samples and correlate the influence of the studied variables of the washing process in the degradation of PLA.

3. Results and discussion

Table 2 shows the full overview of the design of experiments that resulted in the factorial design $2^4$ with the 4 variables and their two levels and, molar mass index (M1/M2) responses. The responses were normalized and scaled in % based on the control sample (PLA) on a scale from 0-100%.
Table 2
Full Design of Experiment considering four variables: \((v_1)\) concentration of sodium hydroxide, \((v_2)\) temperature, \((v_3)\) time, and \((v_4)\) concentration of surfactant.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>(v(1))</th>
<th>(v(2))</th>
<th>(v(3))</th>
<th>(v(4))</th>
<th>M1/M2(x100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>74</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>78</td>
</tr>
<tr>
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<td>70</td>
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<tr>
<td>4</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>72</td>
</tr>
<tr>
<td>5(CP)</td>
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<td>50</td>
<td>10</td>
<td>1.5</td>
<td>80</td>
</tr>
<tr>
<td>6(CP)</td>
<td>1.5</td>
<td>50</td>
<td>10</td>
<td>1.5</td>
<td>81</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>59</td>
</tr>
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<tr>
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<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>76</td>
</tr>
<tr>
<td>10(CP)</td>
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<td>50</td>
<td>10</td>
<td>1.5</td>
<td>81</td>
</tr>
<tr>
<td>11</td>
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<td>-1</td>
<td>1</td>
<td>-1</td>
<td>78</td>
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<td>1</td>
<td>1</td>
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<td>1</td>
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<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>69</td>
</tr>
<tr>
<td>19</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>77</td>
</tr>
</tbody>
</table>

To obtain the results, the combinate variables studied in the PLA washing process and the most important variables, it was calculated the effects from the Equation (5).

Furthermore, the effects of the significant variables were evaluated according to the response surfaces methodology (RSM).

\[
Effect = \bar{Y}_+ - \bar{Y}_-
\]
where $\bar{Y}_+$ and $\bar{Y}_-$ are the mean of the responses of the variables at the high and low levels, respectively.

Through the experiments described in Table 2 it was possible to identify four significative effects: 2 main effects, being only for two individual variables (v3 and v4), and 2 of third order interaction effects (123 and 234) as described in Table 3.

This study aims to analyse how process variables can affect the PLA molar mass ratio (M1/M2) and correlate its effect to the degradative processes. As described in Table 3, the third order interaction of variables v1v2v3 (123), as well as v3 has a negative influence on the process while the third order interaction of variables v2v3v4 (234) and v4 have a positive influence.

<table>
<thead>
<tr>
<th>Variables Interaction</th>
<th>Effect value</th>
</tr>
</thead>
<tbody>
<tr>
<td>v1v2v3 (123)</td>
<td>-6.5</td>
</tr>
<tr>
<td>v3</td>
<td>-3.25</td>
</tr>
<tr>
<td>v4</td>
<td>5.75</td>
</tr>
<tr>
<td>v2v3v4 (234)</td>
<td>7.25</td>
</tr>
</tbody>
</table>

### 3.1. The influence of variables on the molar mass index

#### Influence of negative effects on the PLA washing process

As described in the literature, the use of basic sodium hydroxide solutions and high temperatures is used for pre-decontamination post-consumer packaging before reprocessing [27]. However, the main concern in the PLA washing process is the possibility of degradation by basic hydrolysis catalyzed by high temperatures and excessive exposure time of the material to washing solution [28, 29]. In fact, Table 3 presents the third order interaction effects and the first order variable v3 (washing time), and it can be observed its negative influence on the PLA degradation process, proved by the change of the molar mass index (Table 2). This type of degradation is described as non-intentional chemical recycling as indicated in the work of McKeown et al [20]. Additionally, the authors report that various degradation processes for PLA can occur such as alcoholysis and hydrolysis, leading to the formation of monomers and other compounds non-intentionally added to the material.

Bukersroda et al. [29] described that hydrolysis degradation in biopolymers is influenced by the water diffusion process. Furthermore, a bulk erosion process can occur the higher diffusivity of water permeating the polymer chains, the higher the intramolecular hydrolysis process, leading to a higher molar mass loss. These erosive processes are greatly influenced by the environment in which the
biopolymer is inserted, and two important factors influence the type of erosive process: the pH and the temperature, because both act as catalysts for hydrolysis degradation [29].

In this way, as observed in the response surface of Fig. 1a. the molar mass index (M1/M2) is lower when the third order interaction (v1v2v3) is fixed at its highest level. In the other words, under these conditions there is a greater reduction of molar mass, reaching a value of 41% loss, as observed by the results presented in experiment 7 (Table 2). Moreover, the same result of marked molar mass loss can be observed on the response surface of Fig. 1b. for the first order variable v3 (washing time) when it is at its highest level (1). Consequently, the longer the exposure time of PLA to the washing solution, the higher the molar mass reduction occurs.

Xu and co-workers [28] describe that the hydrolysis degradation process of PLA occurs at temperatures near and below its Tg (~57 ºC). That is because at this temperature the mobility of the polymeric chains of the amorphous phase increases, which facilitates the water diffusion process and directs the hydrolysis degradation mechanism towards the bulk. Therefore, as described above, the temperature and the basic pH of the washing solution act as a catalyst for the degradation process, resulting in the formation of compounds such as oligomers and small molecules, as can be observed in the mechanism proposed in Fig. 2.

**Influence of positive effects on the PLA washing process**

The first order variable v3 has a negative effect on the molar mass as shown in Table 3. However, the same variable has a positive effect on the third order interaction (v2v3v4), influencing the minimization of the degradation process. When the third order interaction is fixed at its highest level (1) and the variable v1 (NaOH concentration) is at its lowest level (-1), there is a smaller molar mass reduction, around 15%, as can be seen in the response surface in Fig. 3.

In addition, from the data obtained by the DoE, and based on the calculation of the effects of the variables, it is possible to modulate and predict the molar mass decrease as a function of the process variables. For example, in the case of the primary variable v4 (surfactant concentration), when it is at the highest level (1) and keeping the other variables at their lowest levels (-1), the molar mass loss can be predicted below 13%. This answer was related to one of the most widely studied topics in the literature, that of the interaction of surfactants and macromolecules which has enabled their use in several industrial applications [30].

The surfactant can interact with the polymer chain by anchoring itself by interactions acting like micelles. This effect occurs when the interaction exceeds the critical aggregation concentration (CAC) [31]. This model of micelles attached to the polymer chain was proposed by Saito and Sata and applied to hydrophobic polymers. However, the model is widely used to describe the chain expansion of hydrophilic polymers interacting with non-ionic surfactants [31]. In this way, the surfactant attached to the polymer chain decreases the hydrolysis degradation process because the water diffusion is hindered by the
micellar behavior of the surfactant that solvates the polymer being observed as a positive effect of the variable v4 as can be seen in Fig. 3.

4. Conclusions

In this study, the application of the Design of Experiments was successfully employed to develop an optimized washing process for the recycling of biodegradable post-consumer PLA packaging. By systematically investigating the effects of various washing parameters and their interactions, it was able to identify the most influential factors and their optimal ranges for achieving a clean and mechanically stable recycled PLA.

The use of Response Surface Methodology (RSM) allowed for a comprehensive understanding of the relationships between the process parameters and response variables.

The conclusions drawn from this study demonstrate the potential of DoE as a valuable tool in the development of sustainable recycling processes for biodegradable packaging materials. By optimizing the recycling process, this investigation contributes to the promotion of a circular economy and reduced environmental impact from packaging waste. Future research may focus on further refining the washing process and expanding the application of DoE to other biodegradable polymers or recycling processes to enhance the sustainability of packaging materials and waste management practices.

Declarations

Funding

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Author Contribution

- S. A. Cruz - responsible for the ideation and conception of the work, as well as for the promotion and discussion at all stages.
- Robert Paiva - executed, discussed and wrote most of the work.
- Edenir Rodrigues Pereira-Filho - both are responsible for the discussion and design of experiment.
- Magdalena Wrona - both are responsible for the discussion and wrote of the work.

Conflict of Interest
The authors confirm that they have no conflicts of interest with respect to the work described in this manuscript.

**Availability of data and material**

All data are the authors' domain and can be requested as soon as the journal requests.

**References**


Figures

![Figure 1](image-url)

**Figure 1**

Response surface for the negative effects of the a) third order interaction \((v_1v_2v_3)\) and the b) primary variable \(v_3\).
Figure 2

PLA degradation mechanisms by basic hydrolysis.

Figure 3

Response surface for the positive effects of the third order interaction (v2v3v4) and the primary effect of the v4 variable.
Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- GA.png