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## ARTICLE

# Organocatalyzed Closed-Loop Chemical Recycling of Thermo-Compressed Films of Poly(ethylene furanoate)

Elena Gabirondo<sup>a</sup>, Beatriz Melendez-Rodriguez<sup>b</sup>, Carmen Arnal<sup>b</sup>, Jose M. Lagaron<sup>b</sup>, Antxon Martínez de Ilarduya<sup>c</sup>, Haritz Sardon<sup>a\*</sup>, Sergio Torres-Giner<sup>b,c\*</sup>

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Monomers obtained from renewable feedstocks have emerged as a sustainable alternative to petroleum derived polymers. One of the biomass derived polyesters that has recently been gaining attention as an alternative to petrochemical polyethylene terephthalate (PET) for food and beverage packaging applications is poly(ethylene furanoate) (PEF). However, similar to PET, PEF is not biodegradable or compostable and its end-of-life options must be thus considered to avoid contributing to the accumulation of plastic waste. In this manuscript, PEF films were first produced using thermo-compression, an industrially relevant processing method, and their thermal, mechanical, and barrier properties were determined and compared to those of PET and other biopolyesters to ascertain their suitability for food packaging. Thereafter, the chemical glycolysis of PEF film waste was investigated using a sustainable and thermally stable acid–base organocatalyst. After successfully deconstructing PEF into bis(2-hydroxyethyl)-furan-2,5-dicarboxylate (BHEF), the obtained BHEF diester was used to resynthesize PEF using the same catalyst to generate a new biopolyester with similar thermal properties to the virgin one in a closed-loop cycle.

## Introduction

There are two main strategic goals in the development of biorefineries: the displacement of petroleum in favor of renewable raw materials and the establishment of a robust bio-based industry, the so-called Bioeconomy.<sup>1</sup> Based on this concept, chemicals from various vegetable feedstocks such as sugars, starch, lignocelluloses, vegetable oils, organic acids or glycerol have been proposed as renewable monomers for polymer production.<sup>2</sup> In particular, the

dehydration of abundant 6-carbon sugars (e.g. fructose and galactose) to give furans is a well-known transformation for the preparation of furfurals such as 5-hydroxymethylfurfural (HMF) and 5-methoxy methyl furfural (MMF) with high selectivity (~80%) and conversion (~90%) rates.<sup>3</sup> The oxidation of HMF, MMF, and their ethers in air over different catalysts<sup>4,5</sup> yields furan-2,5-dicarboxylic acid (FDCA). This furanic compound has been identified as a strategic renewable building block to replace petroleum derived terephthalic acid (TPA) in the production of polyesters.<sup>6</sup> Although the current conversion of furfurals into FDCA only reaches yields of 50–60%, this process is based on mild process conditions and requires low process energy requirements.<sup>7,8</sup>

Petrochemical PET currently has the largest market volume in bottles for water or beverages and it is also widely used in film applications for food trays and lids with a total world production capacity of over 65 million tons of virgin polymer a year.<sup>9</sup> While most PET is derived from petroleum, PET can also be partly bio-sourced at ~30% by using bio-based monoethylene glycol (bio-EG). However, the TPA monomer still remains petroleum derived due to both

<sup>a</sup> Department of Polymer Science and Technology, Institute for Polymer Materials (POLYMAT), Faculty of Chemistry, University of the Basque Country (UPV/EHU), Paseo Manuel de Lardizabal 3, 20018 Donostia, Spain.

<sup>b</sup> Novel Materials and Nanotechnology Group, Institute of Agrochemistry and Food Technology (IATA), Spanish National Research Council (CSIC), Calle Catedrático Agustín Escardino Benlloch 7, 46980 Paterna, Valencia, Spain.

<sup>c</sup> Department d'Enginyeria Química, Universitat Politècnica de Catalunya, Barcelona School of Industrial Engineering (ETSEIB), Diagonal 647, Barcelona, 8028 Spain

\* This author is now with the Research Institute of Food Engineering for Development (IIAD), Universitat Politècnica de València (UPV), Camino de Vera s/n, 46022 Valencia, Spain (storresginer@upv.es)

† Footnotes relating to the title and/or authors should appear here.

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technical and economic constraints.<sup>10,11</sup> Since the production of FDCA and bio-EG utilizes renewable sugars, poly(ethylene 2,5-furandicarboxylate), more commonly termed poly(ethylene furanoate) (PEF), currently represents an appealing bio-mass derived replacement to petrochemical PET.<sup>12</sup> In this regard, Eerhart et al.<sup>13</sup> showed that replacing PET with PEF would reduce the non-renewable energy use by 40–50% and the greenhouse gas (GHG) emissions by 45–55% for the cradle-to-grave system. Therefore, large-scale production of bio-sourced PEF will significantly reduce both greenhouse gas emissions and non-renewable energy usage compared to petroleum-sourced PET.<sup>13</sup>

Despite the fact that FDCA is one of the most stable known monocyclic furan derivatives, its thermal stability is somewhat lower than that of TPA and, hence, it has recently been shown that polymerization conditions must be optimized in order to obtain high molecular weights ( $M_w$ s).<sup>14,15</sup> Melt polycondensation using FDCA and EG yielded  $M_w$  values in the range of 10,000–47,000 g/mol and dispersity ( $\mathcal{D}$ ) of 1.3–2.4. High- $M_w$  PEF has also been obtained by ring-opening polymerization (ROP) using stannous octoate as a catalyst.<sup>16,17</sup> Using ROP, the final  $M_w$  and  $\mathcal{D}$  were 50,000 g/mol and 1.4, respectively. In another study, Knoop et al.<sup>18</sup> produced high- $M_w$  PEF through a two-step process consisting of melt polymerization followed by solid-state polymerization (SSP). This combination of melt polycondensation with SSP has been identified as the best procedure to obtaining high molecular weights.<sup>19–21</sup>

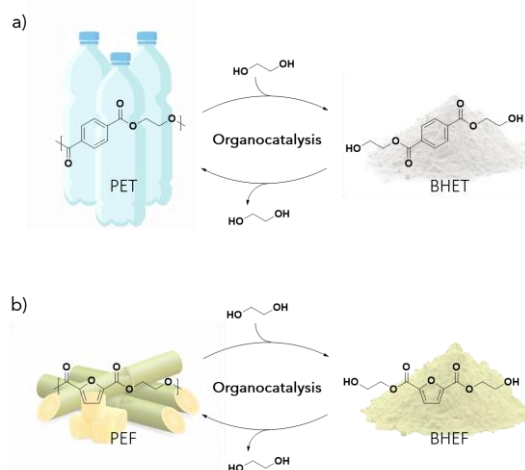
While several studies have dealt with the optimization of the polymerization conditions to obtain high- $M_w$  PEF materials, so far little attention has been paid to the end-of-life assessment of this biopolyester. As in the case of PET, due to the lack of degradation in ambient conditions, mechanical recycling may be the easiest and the cheapest method of recycling PEF. However, as in PET, the number of reprocessing cycles is limited and after recycling the physical properties of the material are diminished.<sup>22,23</sup>

One solution to close the loop of PEF without downcycling the properties is through chemical recycling. This process breaks down plastic waste into raw materials for the production of new high-quality plastics.<sup>24</sup> For instance, it has been shown that PEF-based macrocycles can be recovered when taking advantage of the cyclodepolymerization of PEF at highly diluted conditions. These macrocycles can subsequently be repolymerized into virgin-like materials.<sup>17</sup> While this process can be carried out on a laboratory

scale, its implementation on large scales still needs further development, as much more diluted conditions are required to obtain high yields.

Apart from cyclodepolymerization, like other polyesters, PEF can be depolymerized by solvolysis. For example, Sipos et al.<sup>15</sup> briefly investigated the methanolysis of PEF in the presence of sodium methoxide/methanol solution at 90 °C, but only moderate yields were obtained (~60 %). We envision that using the solvolysis processes, the glycolysis of PEF leading to bis(2-hydroxyethyl)-furan-2,5-dicarboxylate (BHEF) has great potential to close the loop. This process has been already been successfully implemented for PET (Figure 1a).<sup>25</sup>

Herein the preparation and characterization of PEF films and their subsequent chemical recycling to develop a Circular Economy model is reported (Figure 1b). To this end, commercial PEF pellets were shaped into films by thermo-compression and characterized in terms of their mechanical, thermal, and barrier properties to evaluate their potential application in food and beverage packaging. Thereafter, depolymerization of the PEF film waste was carried out by glycolysis using bio-EG and a thermally stable organic catalyst system, yielding the BHEF monomer that was repolymerized into PEF by melt polycondensation.



**Figure 1.** Scheme of the depolymerization by glycolysis and repolymerization using organocatalysts of a) polyethylene terephthalate (PET) and b) poly(ethylene furanoate) (PEF) to yield bis(2-hydroxyethyl) terephthalate (BHET) and bis(2-hydroxyethyl)-furan-2,5-dicarboxylate (BHEF), respectively.

## Experimental

### Materials

PEF was supplied in the form of cylindrical pellets by AVA Biochem BSL AG (Muttentz, Switzerland). According to the manufacturer, its intrinsic viscosity is 0.557 dl/g, weight- and number-average-molecular weights ( $M_w$ ,  $M_n$ ) are 32,600 g/mol and 12,400 g/mol, respectively, resulting in a  $\bar{D}$  value of 2.6. A commercial PET film, with a thickness of approximately 80  $\mu\text{m}$ , of Belectric OPV GmbH (OPVIUS-Organic Photovoltaic Solutions, Kitzingen, Germany) was used as control material. Bio-EG, purum 99.8%, was kindly provided by India Glycols Ltd. (Uttar Pradesh, India). Benzoic acid (BA) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) were purchased from Sigma-Aldrich S.A. (Madrid, Spain) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 98% of purity, was obtained from TCI (Eschborn, Germany) and distilled prior to use. Methanol, hexafluoro-2-propanol (HFIP), deuterated chloroform ( $\text{CDCl}_3$ ), trifluoroacetic acid (TFA), and  $D$ -limonene with 98% purity were all supplied by Sigma-Aldrich S.A. (Madrid, Spain) and used without further purification.

#### Preparation of PEF films

The as-received PEF pellets were dried under vacuum at 80  $^{\circ}\text{C}$  for 12 h in order to remove any residual moisture and, thereafter, thermo-compressed into films using a hot-plate hydraulic press (Carver 4122, Wabash, IN, USA). To this end, the samples were first placed in the plates at 240  $^{\circ}\text{C}$  for 1 minute, without pressure, to remove any the residual moisture and then hot-pressed at 4–5 bars for 2 min. The samples were removed from the press and cooled to room temperature in ambient conditions. Flat films with a thickness of  $\sim 100 \mu\text{m}$  were obtained and stored in a desiccator at 25  $^{\circ}\text{C}$  and 0% RH for, at least, 48 h before characterization.

#### Characterization methods

##### NMR spectroscopy

Proton and carbon nuclear magnetic resonance ( $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR) spectra were collected in a Bruker DPX 300 spectrometer at 300.16 and 75.5 MHz resonance frequencies, respectively. A mixed solvent of  $\text{CDCl}_3$  and TFA at 8:1 (v/v) was used at room temperature. Experimental conditions were as follows: (a)  $^1\text{H}$  NMR spectroscopy: 10 mg of sample; 3 s acquisition time; 1 s delay time; 8.5  $\mu\text{s}$  pulse; spectral width 5000 Hz, and 320 scans. (b)  $^{13}\text{C}$  NMR spectroscopy: 40 mg; 3 s acquisition time; 4 s delay time; 5.5  $\mu\text{s}$  pulse; spectral width 18800 Hz, and more than 10000 scans.

##### MALDI-TOF analysis

Matrix Assisted Laser Desorption Ionization - Time of Flight Mass Spectrometry (MALDI-TOF MS) measurements were performed on a Bruker Autoflex Speed system (Bruker, Germany) instrument, equipped with a 355 nm NdYAG laser using methanol as solvent and DCTB-NaTFA and DCTB-KTFA substrates.

##### Gel permeation chromatography

Gel permeation chromatography (GPC) was performed on a Waters equipment provided with refractive index (RI) and ultraviolet (UV) detectors. For this, 100  $\mu\text{L}$  of 0.1 (wt/vol) sample solution in HFIP was injected and the analysis was performed at a flow-rate of 0.5 mL/min. HR5E and HR2 Waters linear Styragel columns (7.8 mm x 300 mm, pore size  $10^3$ – $10^4$   $\text{\AA}$ ) packed with cross-linked polystyrene (PS) and protected with a pre-column were used. Molar mass averages and distributions were calculated against poly(methyl methacrylate) (PMMA) standards.

##### Thermal properties

Differential scanning calorimetry (DSC) measurements of the thermo-compressed PEF and PET films were performed using a DSC8500 from Perkin Elmer, Inc. calibrated with indium and tin standards. The DSC scans were performed with approximately 5 mg of film sample at a heating rate of 10  $^{\circ}\text{C}/\text{min}$  from -20  $^{\circ}\text{C}$  to 250  $^{\circ}\text{C}$  and subsequent cooling down to 25  $^{\circ}\text{C}$  under a nitrogen flow-rate of 20 mL/min. The percentage of crystallinity ( $X_c$ ) was calculated using Equation 1:

$$X_c = \left[ \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^0} \right] \cdot 100 \quad (\text{Equation 1})$$

Where  $\Delta H_m$  and  $\Delta H_{cc}$  (J/g) correspond to the melting and cold crystallization enthalpies of PEF or PET, respectively, and  $\Delta H_m^0$  (J/g) is the theoretical value of a fully crystalline PEF or PET, which was respectively taken as 137 J/g<sup>26,27</sup> and 140 J/g<sup>13</sup>.

Thermal stability of the films was determined by thermogravimetric analysis (TGA) using a TGAQ500 from TA Instruments under nitrogen atmosphere. Samples of 5–10 mg were heated from 40 to 600  $^{\circ}\text{C}$  at a rate of 10  $^{\circ}\text{C}/\text{min}$ . All thermal tests were performed in triplicate.

##### Mechanical properties

Tensile tests were performed using dumbbell-shaped film samples of PEF and PET sizing 115 mm x 16 mm using a Instron 4400 universal testing machine, equipped with a 1-kN load cell,

from Instron (Norwood, MA, USA) according to the ASTM standard method D638. The tests were conducted using a cross-head speed of 10 mm/min. Samples were conditioned for 24 h prior to analysis and the tests were performed at room conditions, that is, at 40 %RH and 25 °C. A minimum of six specimens was tested.

### Barrier properties

The gravimetric method ASTM E96-95 was used to determine the water vapor permeability (WVP) of the PEF and PET films. Payne permeability cups (diameter of 3.5 cm) from Elcometer Spri (Hermalfsous-Argenteau, Belgium) were filled with 5 mL of distilled water. The films were not in direct contact with water but exposed to 100% RH on one side and secured with silicon rings. They were placed within a desiccator and sealed with dried silica gel at 0% RH and 25 °C. The control samples consisted of cups with aluminum films to estimate solvent loss through the seal. The cups were weighed periodically using an analytical balance ( $\pm 0.0001$  g). WVP was calculated from the regression analysis of weight loss data versus time, whereas the weight loss was calculated as the total loss minus the loss through the seal. The permeability was obtained by multiplying the permeance by the film thickness. The limonene permeability (LP) was measured using a similar method as that for WVP, placing 5 mL of *D*-limonene inside the Payne permeability cups. The cups containing the films were placed at controlled room conditions of 40% RH and 25 °C. The limonene vapor permeation rate (LPRT) values were estimated from the steady-state permeation slopes and the weight loss was calculated as the total cell loss minus the loss through the seal. LP was calculated taking into account the average film thickness in each case. All the WVP and LP measurements were performed in triplicate.

Oxygen permeability (OP) was obtained from the oxygen transmission rate (OTR) measurements, recorded in duplicate, using an Oxygen Permeation Analyzer M8001 from Systech Illinois (Thame, UK) at 23 °C and 0% and 75% RH to simulate both dry and humid packaging conditions. The samples were previously purged with nitrogen in the humidity-equilibrated samples and then exposed to an oxygen flow of 10 mL/min. The exposure area during the test was 5 cm<sup>2</sup>. Sheet thickness and

gas partial pressure were determined. Measurements were performed in duplicate.

### Chemical recycling of PEF films

A similar procedure to that described by Jehanno et. al.<sup>25</sup> for the catalytic degradation of PET was followed. Briefly, 1 g of PEF film was placed with 5 g of bio-EG in the presence of the protic ionic salt of DBU:BA (0.020 g DBU: 0.017 g BA) in a 10 mL schlenk flask. The flask was closed and heated to 180 °C for 2 h under atmospheric pressure and vigorous stirring conditions until complete disappearance of any residual PEF. When the reaction was complete, the crude product was cooled to room temperature and a large excess of distilled water was added. The resulting solution was vortexed and filtered. Thus, the resultant aqueous transparent filtrate was stored at 4 °C in a refrigerator overnight. The precipitate was centrifuged and separated from the solution and finally dried at 40 °C for 24 h.

### Repolymerization of PEF

Polymerization of PEF using the depolymerized product was performed in two steps. The first one consisted of a melt polycondensation step as described by Kasmi et. al.<sup>19,20</sup>, where the monomers react with each other by transesterification reactions and EG units are formed and removed from the media. In this step, low-*M<sub>w</sub>* oligomers were formed. The second step was a SSP process in which the oligomers reacted one with the other to increase the final *M<sub>w</sub>* of the polymer. The first polymerization unit consisted of a 100-mL glass batch reactor with 5 necks that was equipped with a gas inlet, a rotor with a stainless-steel blade, and gas outlet with a Vigreux column heated at 140 °C and connected to a distillation column with an open gas exit and graduated round glass flask. First, 46.7 g of the precipitate obtained from the depolymerization process and 1 g of DBU:BA salt catalyst were charged to the glass reactor. Then, the mixture was purged for 60 min with nitrogen at a flow-rate of 200 mL/min at room temperature to remove the oxygen in the reactor headspace prior to the reaction. The temperature was raised to 170 °C, under nitrogen atmosphere, and the reaction media was stirred at 80 rpm for another 60 min in order to melt the reactant. Once the mixture was homogenized, the pressure was gradually reduced from 200 mbar to 3.4 mbar over 1 h by connecting a vacuum pump

Vacuubrand RZ 2.5 equipped with a VACUU-SELECT® vacuum controller (Vacuubrand GmbH & Co. KG, Wertheim, Germany) to the gas exit and, thereafter, the temperature of the reaction system was slowly raised to 220 °C at 1 °C/min for 1 h under a nitrogen atmosphere to avoid excessive foaming and minimize oligomer sublimation. The reaction was kept at 220 °C for 2 h and stirred at 80 rpm and, finally, cooled to room temperature at room conditions. The viscous mass was removed from the reactor and milled in a IKA A11 basic analytical mill (IKA®- Werke GmbH & Co. KG, Staufen, Germany). The resultant powder was gently washed overnight at room temperature with methanol under vigorous stirring to remove the excess of diol and dried overnight in a vacuum oven (Selecta Vaciotem-T, J.P. SELECTA, Barcelona, Spain) at 80 °C.

In the next step, SSP reaction was carried out in a SSP reactor kindly donated by Prof. Cor Koning (DSM Coating Resins, Geleen, The Netherlands). To this end, 500 mg of PEF oligomer powder was introduced in the SSP reactor and it was purged with nitrogen gas heated at 200 °C at a flow rate of 10 mL/min. Approximately 50 mg of samples were extracted at different times, from 0.5 h to 48 h, and analyzed by <sup>1</sup>H NMR and GPC.

## Results and discussion

### Film characterization

Prior to exploring the chemical recycling of the PEF film, further knowledge about its structure-property relationship was analyzed since it can be of prime interest in the framework of the optimization of its end-use properties in food packaging applications. To do so, the thermal, mechanical, and barrier properties of the thermo-compressed PEF films were determined and compared with those of commercial PET films and also other biopolyesters. Thermo-compression was selected since this melt processing methodology is habitually performed with small samples but it can also be easily scaled up and the results of the films can be compared and transferred to manufacturing processes such as compression molding or injection molding used for high production volumes.

### Thermal Properties

First, the thermal properties of the thermo-compressed commercial PEF film were analyzed and compared to the ones of PET.

**Table 1** shows the main thermal parameters of the films obtained from the DSC thermograms (see **Figure S1**). It can be observed that the amorphous region of PEF showed a  $T_g$  of 84 °C, which is similar to the ones reported by other authors<sup>12,27</sup> and slightly higher than that of the PET used here, (59 °C) and of other studies (76–83 °C).<sup>28</sup> Cold crystallization was not observed at higher temperatures and a sharp endothermic peak was attained at 220.5 °C, corresponding to the melting of the PEF crystals. Therefore, the  $T_m$  value of PEF is lower than that of PET by nearly 25 °C or even more depending on its crystallinity (~250–270 °C).<sup>29</sup> Indeed, compared to PET, PEF usually shows a lower degree of crystallinity and also lower rates of crystallization arising from the difference in geometry between FDCA and TPA.<sup>30</sup> However, herein PEF showed higher crystallinity than PET, 32.1% and 12.9%, respectively, which can be related to the long crystallization time carried out during film formation by thermo-compression as well as the relatively low  $M_w$  of the biopolyester. In any case, the lower  $T_m$  can allow some energy savings in the processing step as lower temperatures will be required. It is worth noting that melting was observed in a single peak, which differs to that reported by both Knoop et al.<sup>18</sup> and Berkel et al.<sup>32</sup> The absence of cold crystallization and the presence of a single melting peak both suggest that PEF developed a more perfect single crystal with a similar lamellae thickness during cooling after thermo-compression.

Thermogravimetric tests were performed on the PEF commercial sample by heating at 10 °C/min under a nitrogen atmosphere and also compared to commercial PET film (see **Figure S2**). In the evolution of mass as function of temperature, it can be observed that PEF degradation occurred in a single step weight-loss process and that the thermal degradation profile of PEF was also similar to that observed for bio-PET, being above 300 °C, though the thermal stability was slightly lower.<sup>26,33</sup>

### Mechanical properties

The mechanical properties of the PEF and PET films and a number of other biopolyesters are shown in **Figure 2**. The averaged values of Young's modulus ( $E$ ) and tensile strength at yield ( $\sigma_y$ ) were  $3364 \pm 95$  MPa and  $83.3 \pm 4.5$  MPa, respectively, while the elongation at yield ( $\epsilon_y$ ) and break ( $\epsilon_b$ ) were  $3.8 \pm 0.8$  % and  $4.1 \pm 0.6$  %, respectively. For the industrial benchmark PET films, lower values of  $E$  and maximum tensile strength ( $\sigma_{max}$ ) have been reported, in the range of 1,000–1,100 MPa and 50–600 MPa, respectively.<sup>34</sup> However, in contrast to

**Table 1.** Thermal properties of the thermo-compressed poly(ethylene furanoate) (PEF) and polyethylene terephthalate (PET) films in term of: glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ), melting enthalpy ( $\Delta H_m$ ), and degree of crystallinity ( $X_c$ ), onset temperature of degradation measured at a mass loss of 5% ( $T_{5\%}$ ), degradation temperature ( $T_{deg}$ ), mass loss at  $T_{deg}$ , and residual mass at 700 °C.

	DSC				TGA			
	$T_g$ (°C)	$T_m$ (°C)	$\Delta H_m$ (J/g)	$X_c$ (%)	$T_{5\%}$ (°C)	$T_{deg}$ (°C)	Mass loss (%)	Residual mass (%)
PEF	84.3 ± 0.2	220.5 ± 2.7	43.97 ± 1.2	32.1 ± 0.8	324.9 ± 2.3	396.7 ± 3.4	56.7 ± 2.2	10.6 ± 0.2
PET	69 ± 1.1	245 ± 2.3	18 ± 0.8	12.9 ± 1.4	405.4 ± 1.9	446.8 ± 4.0	58.3 ± 0.7	1.3 ± 0.1

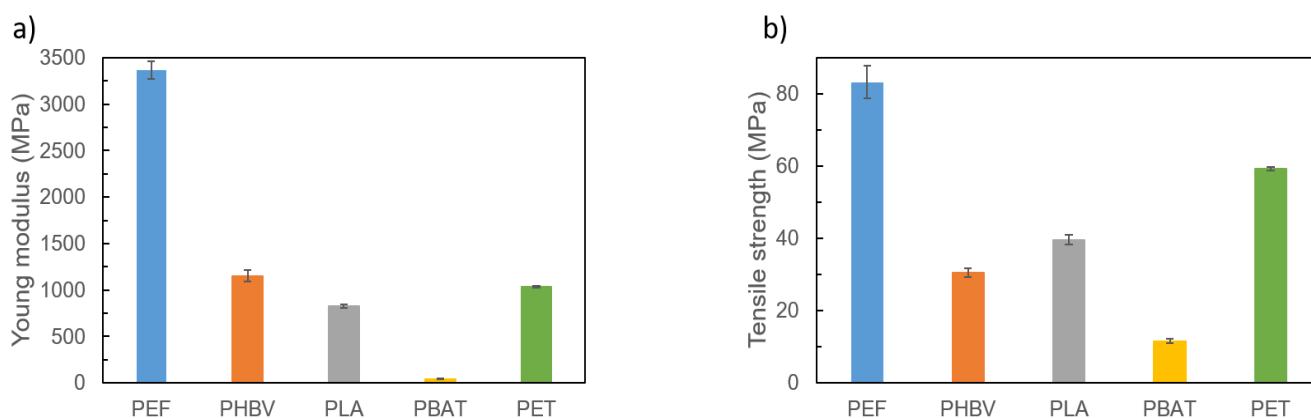
PEF, PET films displayed higher  $\epsilon_b$  values of approximately 50% and 90% for amorphous and semi-crystalline PET, respectively.<sup>34</sup> Therefore, the PEF film displayed brittle behavior, which is further supported from the lack of a yield point in its tensile stress vs. strain curve (see **Figure S3**).

In comparison with other partially or fully bio-based polyesters, such as poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), polylactide (PLA), and poly(butylene adipate-co-terephthalate) (PBAT), the PEF films tested herein are also considerably more elastic and mechanically stronger.<sup>35</sup> Their ductility is in the same range of that of PLA and PHBV, though significantly lower than that of PBAT, which is mostly used in flexible film applications.

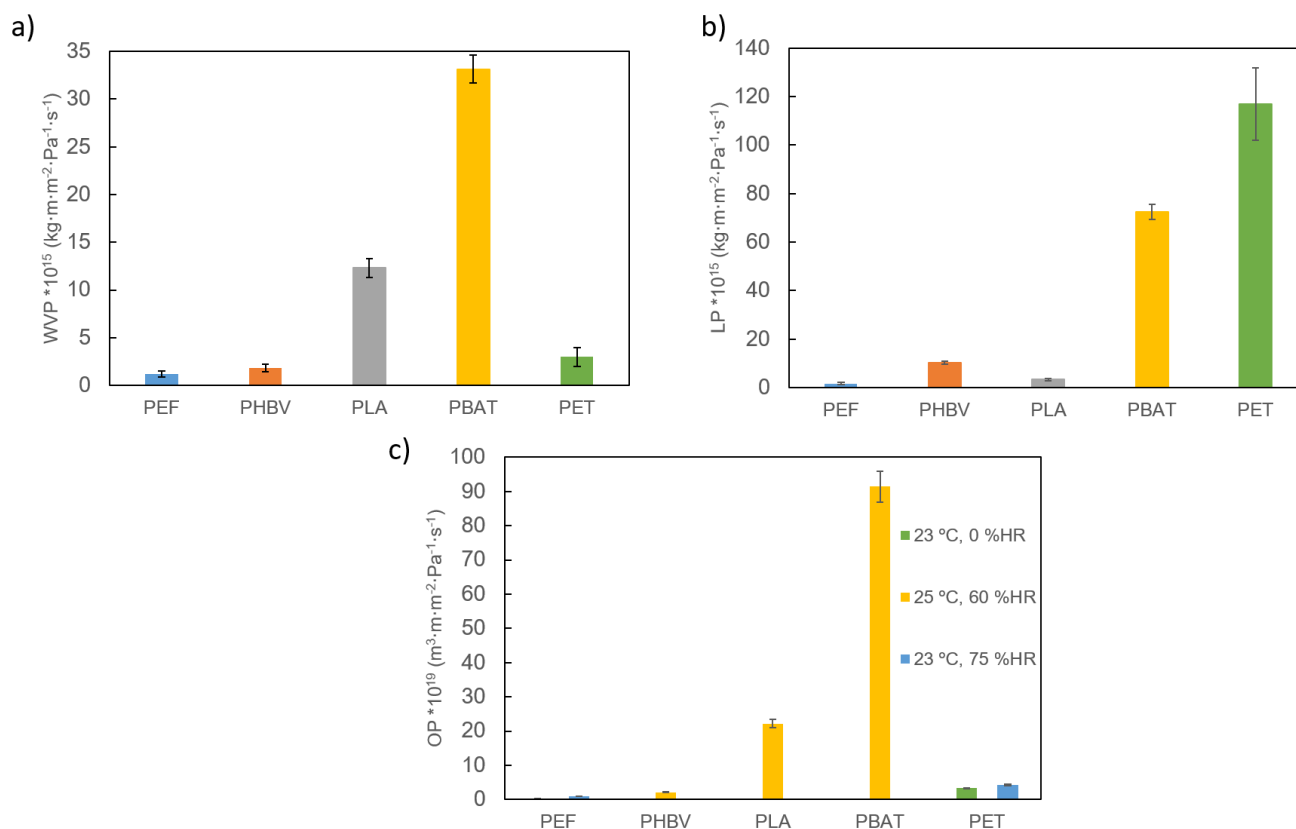
The low ductility of the PEF films used here can be related to the relatively low  $M_w$  of the currently available PEF. Most grades are still under development at the industrial scale or in a pre-market trading stage, and thus PEF biopolymers with higher viscosities and hence lower crystallinity and higher toughness should be expected in a near

future. However, it is also noteworthy that the mechanical properties of the thermo-compressed PEF film showed higher mechanical properties than those of injection-molded pieces prepared by Zhou and coworkers.<sup>36</sup> The slightly higher mechanical properties of the thermo-compressed film in relation to some of the previously developed PEF articles may be related to the PEF grade but also to improved crystallinity during their manufacturing.

In summary, whereas the low ductility of PEF can be limiting for flexible film applications, it can be still useful for rigid articles and high strength fiber applications. It can be particularly interesting for applications where a higher mechanical resistance is needed. Furthermore, the higher elasticity in combination with the higher  $T_g$  would allow for improvement of the thermomechanical stability of the PEF films in comparison to those of PET, such as heat deflection temperature (TDT) or Vicat softening point (VST).



**Figure 2.** a) Young's modulus and b) tensile strength at yield of poly(ethylene furanoate) (PEF), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), polylactide (PLA), poly(butylene adipate-co-terephthalate) (PBAT), and polyethylene terephthalate (PET).



**Figure 3.** Permeability of a) water, b) limonene vapour and c) oxygen gas at for poly(ethylene furanoate) (PEF), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), polylactide (PLA), poly(butylene adipate-co-terephthalate) (PBAT), and polyethylene terephthalate (PET).

### Barrier properties

Besides optimal thermal and mechanical properties, the key parameter for implementing a material in food packaging applications is its response to different permeants such as vapors and gases. **Figure 3** shows the permeability of the thermo-compressed PEF film as well as that of PET and other biopolyesters to water and limonene vapors and oxygen gas. PEF showed a WVP value of  $1.20 \times 10^{-15} \text{ kg}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}\cdot\text{s}^{-1}$ , which is approximately 2.5 times lower than the WVP of PET ( $3.01 \times 10^{-15} \text{ kg}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}\cdot\text{s}^{-1}$ ). The WVP reduction for PEF in comparison to PET falls in the range to that of reported by Avantium<sup>37</sup> and Burgess et al.<sup>38</sup> The aforementioned permeability reduction can be attributed to fundamental differences in segmental mobility that originate from the rigid furan moiety in PEF compared to the mobile phenyl moiety in PET.<sup>12</sup> In comparison with other commercial biopolyesters, the water vapor barrier properties of PEF showed a slight improvement over PHBV ( $1.82 \times 10^{-15} \text{ kg}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}\cdot\text{s}^{-1}$ ) and were significantly superior to PLA ( $12.31 \times 10^{-15} \text{ kg}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}\cdot\text{s}^{-1}$ ) and PBAT ( $33.13 \times 10^{-15} \text{ kg}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}\cdot\text{s}^{-1}$ ).<sup>35</sup> Furthermore, its

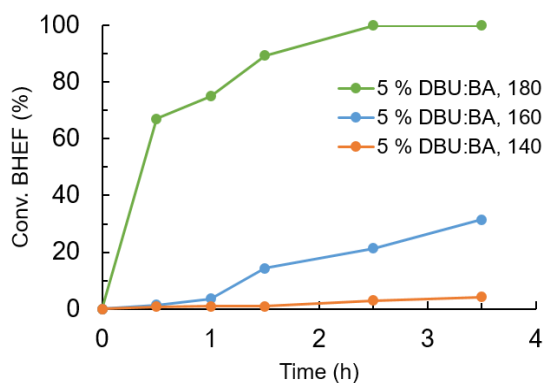
WPV is equivalent to that of low-density polyethylene (LDPE) ( $1.20 \times 10^{-15} \text{ kg}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}\cdot\text{s}^{-1}$ ) and close to that of polypropylene (PP) ( $0.73 \times 10^{-15} \text{ kg}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}\cdot\text{s}^{-1}$ ), some of the standard water barrier polymers used in food packaging applications.<sup>39</sup>

Whereas both water vapor and oxygen barrier properties are important to avoid physical and chemical deterioration, limonene transport properties are usually used as a standard system to test aroma barriers in food packaging. It can be observed that LP of the PEF film was  $1.7 \times 10^{-15} \text{ kg}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}\cdot\text{s}^{-1}$ , which nearly represents a 70-fold reduction in aroma permeability in comparison to PET ( $1.17 \times 10^{-13} \text{ kg}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}\cdot\text{s}^{-1}$ ). This result can be attributed to the fact that the PET film is known to be strongly plasticized by limonene and, thus, loses its dimensional stability.<sup>40</sup> The high barrier of PEF against aroma certainly opens up new uses for food preservation for this biopolymer since it outperforms the barrier properties of current commercial biopolyesters such as PLA ( $3.30 \times 10^{-15} \text{ kg}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}\cdot\text{s}^{-1}$ ), PHBV ( $10.30 \times 10^{-15} \text{ kg}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}\cdot\text{s}^{-1}$ ), and PBAT ( $72.58 \times 10^{-15} \text{ kg}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}\cdot\text{s}^{-1}$ ).<sup>35</sup>



One can also observe that PEF exhibited significantly improved oxygen barrier properties as compared PET. In particular, the OP values of the PEF film were  $3.00 \times 10^{-20} \text{ m}^3 \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$  at 0% RH and  $9.20 \times 10^{-20} \text{ m}^3 \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$  at 75% RH. These conditions were chosen to describe more accurately the dry and humid conditions found in film packaging applications. Compared to PET, the values reported here correspond to a permeability reduction of 10.8 times at 0% RH ( $3.27 \times 10^{-19} \text{ m}^3 \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$ ) and 4.6 times at 75% RH ( $4.26 \times 10^{-19} \text{ m}^3 \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$ ) for oxygen in PEF. The reduction attained in OP at low humidity is similar to that of  $\sim 11$  times reported by Burgess et al.,<sup>12</sup> who explained this improvement primarily by a difference in chain mobility, since both polyesters exhibit similar oxygen solubilities at 35 °C. Furthermore, the higher crystallinity attained in the thermo-compressed PEF films could also contribute to the high gas barrier properties. Finally, the PEF films also outperformed the oxygen barrier properties of films made of PLA, PHBV, and PBAT ( $2.22$ ,  $0.21$ , and  $9.14 \times 10^{-18} \text{ m}^3 \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{Pa}^{-1} \cdot \text{s}^{-1}$ , respectively, measured at 60% RH).<sup>35</sup>

The low permeability values for water, aroma and, more notably, oxygen further confirms the notion that PEF can potentially serve as a viable alternative to PET in the beverage market. Nevertheless, the significant oxygen barrier improvements for PEF compared to PET greatly expand the opportunities for introduction of PEF into markets beyond that of beverage applications such as barrier food packaging, particularly at low moisture conditions. Furthermore, the overall high barrier performance in terms of water and limonene vapors and oxygen gas makes PEF a great candidate for monomaterial packaging. This notion is complemented by PEF exhibiting improved mechanical strength but lower ductility and thermal properties compared to PET.

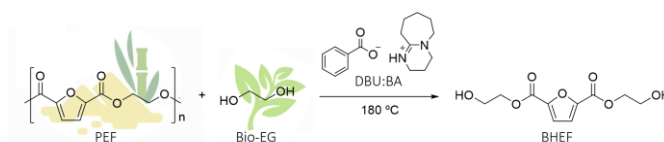


**Figure 5.** a) Influence of the temperature in the conversion speed and b) influence of the amount of 1,8-diazabicyclo[5.4.0]undec-7-ene:benzoic acid (DBU:BA) catalyst in the conversion.

## Chemical Recycling of PEF film

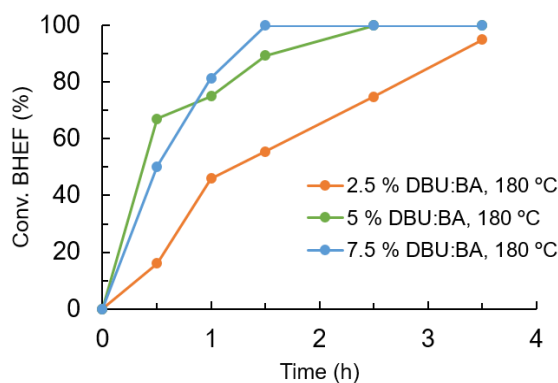
As shown above, PEF offers excellent properties for food packaging applications and the production of this biopolyester represents an effective biomass derived replacement to the petrochemical PET. However, sustainable end-of-life options should be sought for PEF in order for it to become a viable alternative to PET since both polyesters are neither biodegradable nor compostable. Considering the current low production of PEF, chemical recycling is foreseen to be the best sustainable solution.

In this regard, the chemical glycolysis of PEF using bio-EG in combination with different catalysts was performed at 180 °C. The catalysts that were explored consisted of DBU, TBD, BA, and the protic ionic salt DBU:BA. As shown in **Figure 4**, the expected product of the reaction is BHEF, which is similar to the bis(2-hydroxyethyl) terephthalate (BHET) monomer obtained from the depolymerization of PET.<sup>25</sup>



**Figure 4.** Depolymerization reaction of commercial polyethylene furanoate (PEF) with bio-based monoethylene glycol (bio-EG) and catalyzed by 1,8-diazabicyclo[5.4.0]undec-7-ene:benzoic acid (DBU:BA) to yield the bis(2-hydroxyethyl)-furan-2,5-dicarboxylate (BHEF) monomer.

Results showed that the acid, that is, BA, was not able to depolymerize PEF into the BHEF monomer. Both basic catalysts, DBU and TBD, gave the desired product with yields of 55% and 72%, respectively, whereas DBU:BA resulted in 92% of yield (see **Figure**

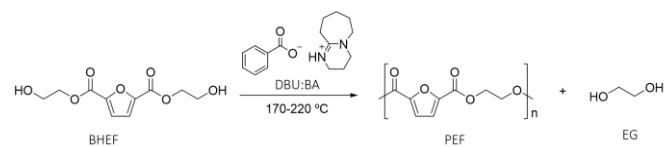


**S4**). The catalyst DBU:BA is an acid-base mixture that combines the excellent catalytic ability of organic compounds with the thermal stability of metal-based catalysts, resisting degradation up to >250 °C, and it has shown to be efficient to depolymerize PET.<sup>41,42</sup> As the catalyst is soluble in water, it could be easily removed and recovered in the purification step and, thus, it could be reused. As shown in **Figure 5**, the reaction was completed in nearly 2.5 h, slightly slower than for PET,<sup>25</sup> when using 5 wt% of organocatalyst at 180 °C. It was observed that at lower temperatures the reaction was considerably slower. With higher organocatalyst contents (7.5 wt%), the reaction was completed slightly faster, but without any significant improvement, while at 2.5 wt% of organocatalyst the reaction was significantly slower. The kinetic data resulted in an activation energy ( $E_a$ ) of 163 kJ/mol, which justifies the relatively high temperatures required to successfully depolymerize PEF.

The final product resulting from depolymerization was analyzed using <sup>1</sup>H NMR and MALDI-TOF spectroscopy. Resonances in the <sup>1</sup>H NMR spectrum of the reaction product were at  $\delta = 4.0$ , 4.5, and 7.3 ppm, which are assigned to the ester linkage and confirmed the formation of BHEF (see **Figure S5**). The peaks at 4.0 and 4.5 ppm belong to EG monomer when attached to the furanoate and the signal at 7.3 ppm to the furanoate ring. The additional low-intensity resonance seen at 4.7 ppm indicates that other products than the desired BHEF were also formed, most likely corresponding to BHEF oligomers. In order to determine the presence of other species different from BHEF, the samples were further analyzed using MALDI-TOF spectroscopy. As found in the MALDI-TOF spectrum, together with the monomer, the BHEF dimer was also observed (see **Figure S6**). As the final goal was focused on the repolymerization of the obtained BHEF into PEF, monomer and dimer were not separated.

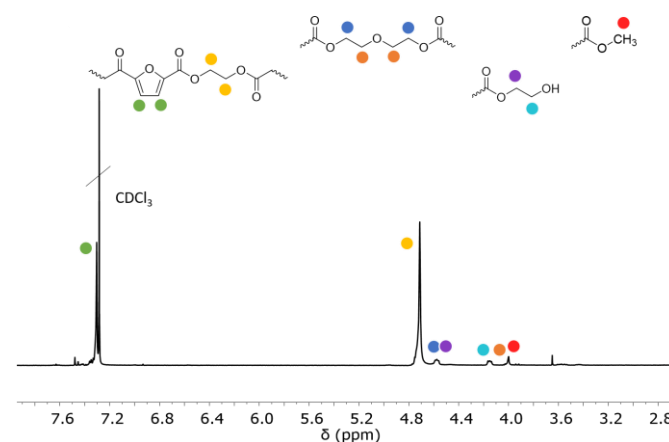
After successfully achieving the chemical recycling of the PEF film, the obtained BHEF was investigated as a source to produce PEF by polycondensation. It was envisaged that BHEF would enable the repolymerization of PEF polymer by self-polycondensation as proposed in the scheme reaction of **Figure 6**. As in the case of PET, the BHEF monomer will enable the preparation low- $M_w$  PEF by melt condensation. In each condensation, a molecule of EG is released and needs to be removed from the reaction media in order to promote the synthesis of the biopolymer so that both vacuum and high

temperatures are required. The process was performed using the same organocatalyst as for the depolymerization, that is, the DBU:BA mixture, and the temperature was gradually increased from 170 to 220 °C and vacuum from 200 to 3.4 mbar to minimize sublimation of the monomer.<sup>43</sup>



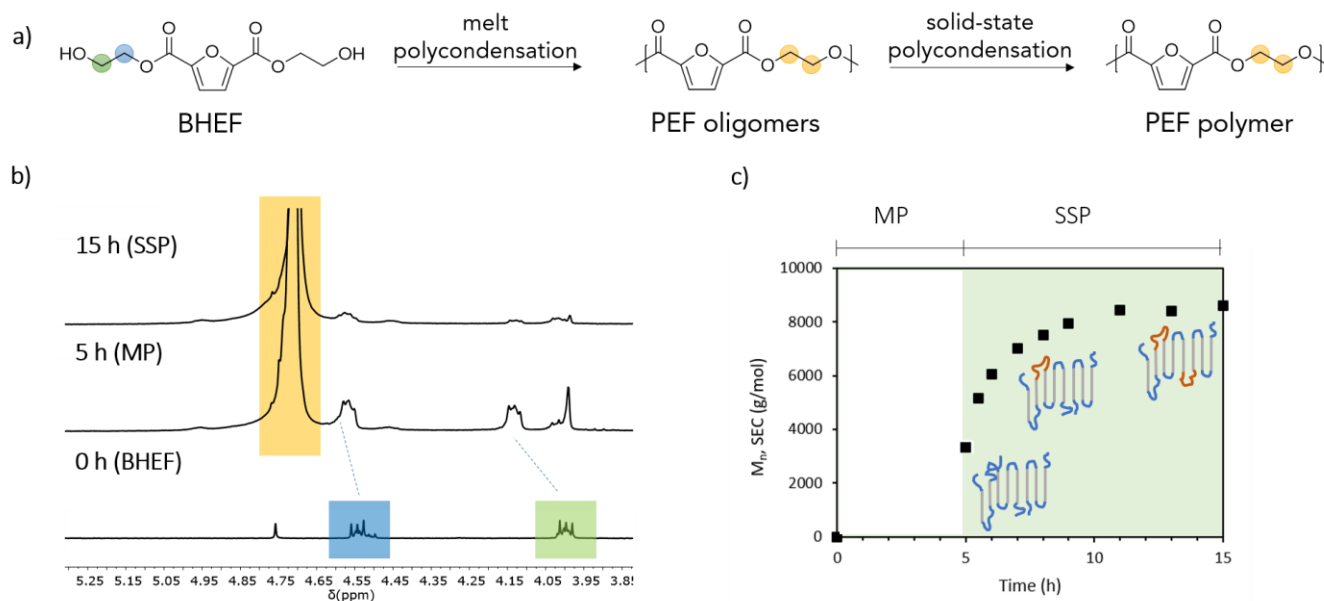
**Figure 6.** Melt polycondensation of poly(ethylene furanoate) (PEF) starting from bis(2-hydroxyethyl)-furan-2,5-dicarboxylate (BHEF).

**Figure 7** shows the <sup>1</sup>H NMR spectrum of the melt-polycondensed product from BHEF. One can observe strong signals at 7.3 and 4.7 ppm that correspond to the furanoate ring and the ethylene glycol unit, respectively, when they are linked by an ester bond. The <sup>1</sup>H NMR spectrum reported by Gandini et al.<sup>44</sup> for PEF in deuterated trifluoroacetic acid (d-TFA or CF<sub>3</sub>COOD) showed resonance of the H3 and H4 furan protons at 7.43 ppm, and that of the ester CH<sub>2</sub> at 4.78 ppm with the expected 1:2 integration ratio. After this first step, the attained  $M_w$ s were relatively low (up to 8,450 g/mol).



**Figure 7.** Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectrum of the reaction product from the melt polycondensation of the depolymerized poly(ethylene furanoate) (PEF).

In order to obtain higher  $M_w$ s, SSP was performed in a second stage using the material obtained from melt polymerization. In this process, the previously synthesized oligomers were treated using four different temperatures, that is, 100, 170, 190, and 200 °C. Polymerization did not occur at 100 °C, and the  $M_w$  was the same as the one obtained by melt polymerization (see **Figure S7**). The other



**Figure 8.** a) Synthesis process of poly(ethylene furanoate) (PEF) from bis(2-hydroxyethyl)-furan-2,5-dicarboxylate (BHEF) in two stages: melt polycondensation (MP) and solid-state polycondensation (SSP); b) Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra of the reaction kinetics; c) number average-molecular weight ( $M_n$ ) evolution during the synthesis determined by size-exclusion chromatography (SEC).

temperatures led to an increase in  $M_w$ , however the optimum temperature was attained at 200 °C. This temperature is above the  $T_g$  and below the  $T_m$  of PEF (see **Table S1**), there it can promote the growth of the chain in the amorphous regions of the oligomers. This post-condensation technique is environmentally benign compared to conventional melt polycondensation, as it is a solvent-free method and no toxic waste is released during the polymerization.<sup>21</sup> The kinetics of the polymerization reaction was followed by  $^1\text{H}$  NMR and GPC analysis, as shown in **Figure 8 a & b**. The evolution of  $M_n$ ,  $M_w$ ,  $\bar{D}$ , and the dimerization of PEF was analyzed over time during SSP (see further details in **Figures S8** and **S9**). It was observed that SSP at 200 °C led to higher  $M_w$ s ( $M_n = 11,200$  g/mol,  $M_w = 38,000$ , and  $\bar{D} = 3.4$ ) than at lower temperatures. These parameters are comparable with those of commercial PEF ( $M_n = 12,400$  g/mol,  $M_w = 32,600$  g/mol, and  $\bar{D} = 2.6$ ). During the SSP process, the concentration of the biopolymer chains and the mobility of the end-group were enhanced. The overall increase of  $M_w$  with long times is due to the elimination of by-products formed during SSP, which follows a diffusion-controlled mechanism.<sup>19</sup> One can also notice that  $\bar{D}$  remained in the range 2.0–2.6 for the first 8 h of reaction and, thereafter, it significantly increased up to 3.6 and 3.4 after 24 and 48 h, respectively. It is also worth highlighting that the dimerization, which indicates the degree of EG that dimerized (see **Figure S10**), was kept below the 1.8–2.2% range, being slightly lower than that attained in the commercial PEF

sample (2.3 %). This observation can be related to the fact that SSP was implemented under relatively mild conditions and, therefore, fewer side reactions and thermal degradation could occur.<sup>18,20,21</sup> Finally, the depolymerization of the repolymerized PEF was carried out following the procedure that was used for the commercial one, obtaining the same yield, that is, 92 % of BHEF product (see **Figure S11**).

The oligomer and polymer obtained after each step were also compared with the commercial PEF by DSC (see **Figure S12**). The oligomers that were synthesized after the melt polymerization (labeled as “PEF 5h”) showed lower  $T_g$  (~85 °C) and  $T_m$  (~210 °C) values than the commercial polymer due to their reduced  $M_w$  and higher monomer content. After SSP (“PEF 15h”), the transition temperatures increased, resulting in a  $T_g$  value of nearly 87 °C and a  $T_m$  of 224 °C. These values are in the range of that of commercial PEF, which showed a  $T_g$  of 93 °C and a  $T_m$  of 213 °C, confirming the successful recycling of PEF from its depolymerization and subsequent repolymerization of BHEF.

## Conclusions

In this work, the suitability of bio-based PEF for food packaging applications using an industrially relevant film-processing method was studied. After physical characterization and comparison with

PET and some biodegradable polyesters, the depolymerization of commercial PEF was carried out by glycolysis using a bio-based glycol, bio-EG, and a thermally stable organocatalyst, DBU : BA. After investigating and monitoring different depolymerization conditions, the depolymerization products were analyzed using  $^1\text{H-NMR}$  and MALDI, confirming the synthesis of BHEF monomer and dimer. The obtained recycled monomers were finally repolymerized by melt polycondensation followed by SSP to get virgin-like PEF. The easy depolymerization process and the further repolymerization step can offer a sustainable end-of-life option for PEF to facilitate its industrial implementation in the Circular Economy frame.

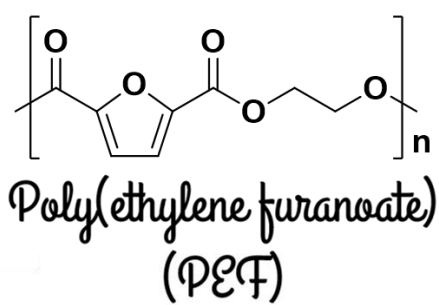
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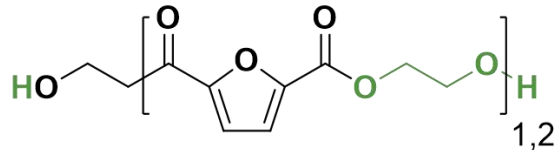
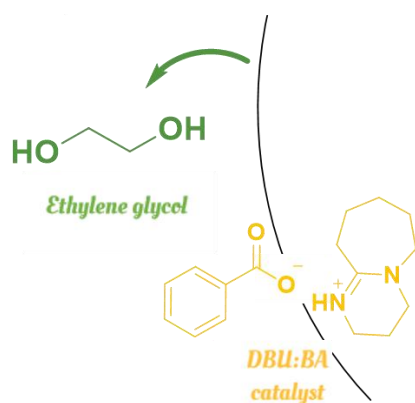
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### Repolymerization



### Depolymerization

