



ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

ARCHIVIO ISTITUZIONALE
DELLA RICERCA

Alma Mater Studiorum Università di Bologna Archivio istituzionale della ricerca

Bio-based and one-day compostable poly(diethylene 2,5-furanoate) for sustainable flexible food packaging:
Effect of ether-oxygen atom insertion on the final properties

This is the final peer-reviewed author's accepted manuscript (postprint) of the following publication:

Published Version:

Quattrosoldi S., Guidotti G., Soccio M., Siracusa V., Lotti N. (2022). Bio-based and one-day compostable poly(diethylene 2,5-furanoate) for sustainable flexible food packaging: Effect of ether-oxygen atom insertion on the final properties. CHEMOSPHERE, 291(Part 2), 1-11 [10.1016/j.chemosphere.2021.132996].

Availability:

This version is available at: <https://hdl.handle.net/11585/852086> since: 2022-02-21

Published:

DOI: <http://doi.org/10.1016/j.chemosphere.2021.132996>

Terms of use:

Some rights reserved. The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>).
When citing, please refer to the published version.

(Article begins on next page)

1 **Bio-based and one-day compostable poly(diethylene 2,5-furanoate) for**
2 **sustainable flexible food packaging: effect of ether-oxygen atom insertion on the**
3 **final properties**

4

5

6 *Silvia Quattrosoldi ^{a,s}, Giulia Guidotti ^s, Michelina Soccio ^{a,*}, Valentina Siracusa ^b, Nadia Lotti ^{a,r,d}*

7

8

9 ^aCivil, Chemical, Environmental and Materials Engineering Department, University of Bologna,

10 Via Terracini 28, 40131 Bologna, Italy

11 ^bChemical Science Department, University of Catania, Viale A. Doria 6, 95125 Catania, Italy

12 ^cInterdepartmental Center for Industrial Research on Advanced Applications in Mechanical

13 Engineering and Materials Technology, CIRI-MAM, University of Bologna, Bologna, Italy

14 ^d Interdepartmental Center for Agro-Food Research, CIRI-AGRO, University of Bologna, Bologna,

15 Italy.

16

17

18

19 **Keywords:** 2,5-furandicarboxylic acid; ether linkage; barrier properties; mechanical properties;

20 compostability

21 § These authors contributed equally.

22 **Abstract**

23 In the present work, the effect of ether oxygen atom introduction in a furan ring-containing polymer
24 has been evaluated. Solvent-free polycondensation process permitted the preparation of high
25 molecular weight poly(diethylene 2,5-furandicarboxylate) (PDEF), by reacting the dimethyl ester of
26 2,5-furandicarboxylic acid with diethylene glycol. After molecular and thermal characterization,
27 PDEF mechanical response and gas barrier properties to O₂ and CO₂, measured at different
28 temperatures and humidity, were studied and compared with those of poly(butylene 2,5-
29 furandicarboxylate) (PBF) and poly(pentamethylene 2,5-furanoate) (PPeF) previously determined.
30 Both PDEF and PPeF films were amorphous, differently from PBF one. Glass transition temperature
31 of PDEF (24 °C) is between those of PBF (39 °C) and PPeF (13 °C). As concerns mechanical
32 response, PDEF is more flexible (elastic modulus [E] = 673 MPa) than PBF (E = 1290 MPa) but stiffer
33 than PPeF (E = 9 MPa). Moreover, PDEF is the most thermally stable (temperature of maximum
34 degradation rate being 418 for PDEF, 407 for PBF and 414 °C for PPeF) and hydrophilic (water
35 contact angle being 74 ° for PDEF, 90 ° for PBF and 93 ° for PPeF), with gas barrier performances
36 very similar to those of PPeF (O₂ and CO₂ transmission rate being 0.0022 and 0.0018 for PDEF and,
37 0.0016 and 0.0014 cm³ cm / m² d atm for PPeF). Lab scale composting experiments indicated that
38 PDEF and PPeF were compostable, the former degrading faster, in just one day.
39 The results obtained are explained on the basis of the high electronegativity of ether oxygen atom
40 with respect to the carbon one, and the consequent increase of dipoles along the macromolecule.

41

42

43 **1. Introduction**

44 Although relatively new compared to wood, glass and metals, these last used by man since the dawn
45 of time, plastics have been used more and more and today they are practically irreplaceable. As proof
46 of this, their production has increased from 270 million metric tons to almost 370 million metric tons
47 from 2010 to 2020, and it is expected to further increase, rising to about 590 million metric tons by
48 2050.^{1,2} Their global market is also expected to reach 750.1 billion of dollars by 2028.³ Such a
49 massive use of plastics entails a significant impact on both exploitation of non-renewable sources and
50 on accumulation of wastes in the marine and terrestrial habitats. The environmental problems caused
51 by human activity are one of the main themes of debate of the last Century. With the perspective of
52 reducing the environmental issues and building a new circular economy, the employment of
53 renewable resources for plastic production and plastic waste recycling are the most suitable solutions.
54 For this reason, sustainable materials are attracting a continuously growing interest as potential
55 candidates for the replacement of traditional plastics.^{4,5} To date, promising results have been obtained
56 with bioplastics, in particular with the class of bio-based polyesters.^{6,9} Their bio-based nature makes
57 them particularly interesting for applications in food packaging field, since the multilayer structure
58 of most of the packaging currently used creates severe recycling limits.¹⁰ Nevertheless, to be suitable
59 for food packaging employment, a polymeric device has to satisfy strict requirements, including
60 proper mechanical response and outstanding barrier performance.¹¹ Nowadays, the so-called “smart
61 packaging” has attracted a great interest too, as a result of lifestyle changes and consumer’s desire for
62 convenient, safe and tasty food with prolonged shelf life and unaltered quality and freshness.^{12,13} In
63 these intelligent packaging systems, added materials interact with the internal environment of the
64 package, monitoring the state of the food inside and reducing its corruption until consuming.¹⁴⁻¹⁶
65 Another way to reduce environmental impact, is the use of flexible packaging instead of rigid one. A
66 LCA study commissioned by Flexible Packaging Europe in 2021 showed that flexible packages have

67 a more than 60% lower impact than their rigid counterparts.^{17,18} More in detail, using flexible
68 alternatives means reducing package volumes and amount, saving space and energy during
69 transportation and minimizing wastes. As a confirmation of this, another study, carried out by the
70 Institute for Energy and Environmental Research in 2020, demonstrated that flexible packaging is
71 more effective than rigid one in preserving resources and reducing carbon footprint: if all rigid
72 packaging of non-beverage Fast Moving Consumer Goods in the European Union would be substitute
73 by flexible one, the amount of primary packaging waste could be reduced by 21 million tonnes (i.e.
74 70%) per year.¹⁸

75 In this framework, furan-based polyesters can be surely considered the materials of the future,¹⁹⁻²⁴
76 since they can be used to produce a mono-material packaging, combining bio-based origin²⁵⁻³¹ with
77 excellent barrier properties and tunable mechanical performances, ranging from high stiffness to
78 elastomeric behavior.^{32,33} More important, they can also be recycled, once the first use has been
79 accomplished.

80 When employed as food containers, plastics are often contaminated with organic matter, which
81 prevents recycling, or at least makes it very expensive,. Moreover, it must be kept in mind that an
82 efficient and sustainable plastic waste management became more complex and difficult due to
83 COVID-19.^{34,35} The pandemic emergency , has determined a huge increase of food packaging plastic
84 waste due to online shopping and home delivery, accompanied by a change in mindset, according to
85 which single use plastics provides “safety”. Plastic recycling increased at slower rate for fear that
86 plastic wastes might be infected, and due to the lockdown too.³⁶

87 Within this scenario, which was already complex and became even more difficult due to the
88 pandemic, compostable packaging represents the best option, especially for single-use plastics.

89 Aromatic polymers, such as furan-based polyesters, are hardly attacked both by water and/or
90 microorganisms.³⁷⁻⁴⁰ The development of a strategy able to enhance their modest degradation rate is
91 a really important challenge.^{41,42}

92 As is well known, the strong point of plastics is the unique combination of light weight, durability,
93 low cost, ease of synthesis and the possibility to *ad hoc* modify their functional properties in view of
94 the particular application. Even though the use of additives, physical and chemical blending and
95 production of composites are very effective tools to properly tune the material performances,^{24,43,44}
96 the starting point is definitely represented by a proper chemical design. Minor modifications in the
97 chemical structure of a polymer, such as the overall composition, the atomic arrangement in the
98 backbone, the length of the subunits in the repeating unit, the presence of side-groups and isomerism
99 can lead to significant variations in physical properties.^{21,22,45-49} Macromolecular mobility and the
100 developed microstructure are strongly connected to the chemical structure of the polymer, thus
101 affecting features like mechanical response, thermal stability, hydrophilicity, gas barrier performance
102 and compostability.⁵⁰

103 Considering also that 2,5-furandicarboxylic acid (FDCA) is one of 12 high value-added chemicals
104 obtained from sugars^{31,51} according to the United States Department of Energy (updated in 2020),^{52,53}
105 in the present work, a new 100% renewable furan-based polyester was synthesized by two-step melt
106 polycondensation reaction, following the “Green chemistry” principles. For this purpose, FDCA has
107 been coupled with diethylene glycol, recently proposed as bio-based monomer,⁵⁴ obtaining
108 poly(diethylene 2,5-furanoate) (PDEF). It is worth noting that the starting monomers, FDCA and
109 diethylene glycol, can be derived from second and third generation cellulosic feedstocks (non-food
110 crops, waste materials and algae), thus avoiding the exploitation of food and animal feed as well as
111 of land destined for food production.⁵⁵ As one can see from the PDEF chemical formula (**Scheme**
112 **1A**), an ether-oxygen atom is contained in its repeating unit. As previously evidenced for other
113 polymeric systems,⁵⁶⁻⁶³ the presence of -C-O-C- moiety in the polymer backbone has several effects,
114 such as an increase in crystallinity degree decrease and wettability. These factors can potentially
115 favour the water/polymer affinity and, consequently, the hydrolytic and bacterial attack of the
116 macromolecule backbone. From the chemical structure point of view, PDEF can be considered as
117 coming from the modification of the previously studied poly(butylene 2,5-furanoate) (PBF)^{33,64} and

118 poly(pentamethylene 2,5-furanoate) (PPeF).^{32,33} In particular, PDEF can be obtained through the
119 insertion of an O atom (centrally located) in the glycol moiety of PBF, or by substituting the central
120 methylene group of the aliphatic subunit of PPeF with the ether-oxygen (**Scheme 1A**). To the best of
121 our knowledge, PDEF was previously synthesized by Katia Loos' group using a lipase as catalyst,⁶⁵
122 and by Haernvall et al. through direct esterification, and characterized from the molecular, thermal
123 and enzymatic degradation point of view.⁶⁶ In addition to molecular and thermal characterization, the
124 polyester reported in the present paper was also subjected to mechanical characterization and the
125 surface hydrophilicity of the compression molded film was also evaluated. Lab-scale composting
126 experiments were carried out at 58°C at 90% humidity. Barrier performances to oxygen and carbon
127 dioxide were investigated at two different temperatures (23 and 38 °C). The effect of relative humidity
128 at 23°C was also studied. All the results obtained for PDEF were compared with the previous ones
129 got on PBF and PPeF with the aim to evaluate the effect of this chemical modification on the final
130 solid-state properties. The present work is meant to enlarge the furan-based polymer knowledge and,
131 more importantly, to lay the foundations for a deep study of structure-property relationship, which is
132 fundamental for the design of new materials addressing the desired final properties.

133

134 **2. Materials and methods**

135 **2.1 Materials**

136 Dimethyl furan-2,5-dicarboxylate (DMF) (99%), diethylene glycol (DEG) (99%), titanium
137 tetrabutoxide (TBT), and titanium isopropoxide (TIP) were reagent-grade products. All reagents were
138 bought from Sigma-Aldrich, except DMF, which was supplied by Matrix Fine Chemicals.

139 **2.2 Synthesis**

140 Poly(diethylene 2,5-furanoate) (PDEF) was synthesized through a green solvent-less two-stage
141 polycondensation process. The reagents DMF (0.031 mol, 5.71 g) and DEG (0.062 mol, 6.58 g), in a
142 molar ratio of 1:2, were charged in a 200 mL glass reactor, together with the catalysts TBT and TIP

143 (200 ppm of both). The system was continuously stirred (50 rpm) and the temperature adjusted by a
144 silicone oil bath. A condenser cooled by liquid nitrogen was coupled to the reactor. In the first step,
145 carried out at 180 °C and under nitrogen flow, the transesterification reactions took place and
146 methanol was released off. After 90% of theoretical methanol was collected (i.e. 90 minutes), the
147 pressure was progressively reduced to 0.05 mbar, while the temperature was raised up to 230 °C. In
148 the second stage, lasting 3 hours, the reaction mass viscosity increased till a constant torque value.
149 Afterwards, the polymer (6.5 g, 95% yield) was discharged from the reactor. A lightly coloured
150 rubber-like solid was obtained. PBF and PPeF were previously synthesized by the authors through
151 the same polycondensation procedure using the same catalysts.^{32,33} Briefly, for PBF the glycolic
152 molar excess was 300%, the first step was carried out at 180°C for 3 hours and the second one at
153 230°C for further 3 hours. In case of PPeF, a glycolic molar excess of 500% was adopted, the first
154 step was carried out at 170°C for 3 hours while the second one at 220°C for further 2.5 hours.
155 The as-synthesized polymer was solubilized in chloroform and then precipitated in cold methanol, in
156 order to remove residual catalysts and low molecular weight by-products.

157 **2.3 Molecular characterization**

158 Polymer chemical structure was verified by ¹H-nuclear magnetic resonance spectroscopy (Varian
159 Inova 400-MHz Instrument) at room temperature using deuterated chloroform (CDCl₃) as solvent.
160 The solution contains also 0.03 vol% tetramethylsilane (TMS) as an internal standard. The
161 concentration of the polymeric solution was 0.5 wt %.

162 Polymer number molecular weight (M_n) and polydispersity index (\mathcal{D}) were determined by a 1100
163 HPLC system (Agilent Technologies) equipped with PLgel 5 mm MiniMIX-C column, at 30 °C.
164 Chloroform was used as the eluent, 0.3 mL/min flow, and sample concentrations of about 2 mg/mL
165 were adopted. Calibration curve was obtained using polystyrene standards in the range of 800–
166 100000 g/mol.

167 **2.4 Thermal characterization**

168 Differential Scanning Calorimetry (Perkin Elmer DSC6), calibrated with indium and cyclohexane
169 standards, was used to analyse the thermal transitions by heating from -70 °C to 190 °C at 20 °C/min
170 (I scan, resolution: 0.1 seconds between points). The sample (5 mg) was then cooled to -70 °C at 100
171 °C/min, and after that another heating scan was performed (II scan, resolution: 0.1 seconds between
172 points). The glass transition temperature (T_g) and heat capacity (Δc_p) were taken as the midpoint and
173 the height, respectively, of the heat capacity step at the glass transition. Melting temperature (T_m) and
174 crystallization temperature (T_{cc}) were determined as the peak maximum/minimum of the
175 endothermic/exothermic phenomena in the I and II heating scan DSC curves, respectively. The
176 corresponding heat of fusion (ΔH_m) and heat of crystallization (ΔH_{cc}) were obtained from the total
177 area of the DSC endothermic and exothermic signals, during the I and the II heating scans,
178 respectively. For the determination of ΔH_m and ΔH_{cc} we have used a straight baseline.

179 Thermogravimetric analysis (Perkin Elmer TGA7), was employed to evaluate the thermal stability
180 by heating 5 mg of polymer from 50 to 800°C at 10°C/min under nitrogen atmosphere (gas flow: 40
181 ml/min). The maximum degradation rate temperature (T_{max}) was calculated as the minimum of
182 thermogram derivative .

183 **2.5 Film preparation**

184 Polymer films (2.5 g, 11 x 11 cm², 100 µm thickness) were obtained by compression molding the
185 synthesized material with a laboratory press Carver C12. The polymer was heated to 100 °C, kept
186 under 5 ton/m² pressure for 2 min, removed from the press and left cooled down to room temperature.
187 Then, the films were stored at room temperature for 30 days before further characterization.

188 **2.6 Water contact angle measurements**

189 Water contact angle (WCA) determination was carried out on the compression moulded films using
190 a KSV CAM101 instrument (Helsinki, Finland) at room temperature. The side profiles of deionized
191 water drops (4 µL) on the polymer surface were analyzed just after deposition. In case of PDEF, also

192 the drop shape evolution with time was considered. At least 10 tests have been performed on different
193 film areas, from which the WCA average value \pm standard deviation was determined.

194 **2.7 Mechanical characterization**

195 Tensile tests were performed on rectangular specimens (5 mm x 50 mm x 100 μ m) by means of an
196 Instron 5966 testing machine with a transducer-coupled 1kN load cell (stretching rate: 10 mm/min).
197 The measurements were carried out at room temperature (23 °C) and a relative humidity of 55%.
198 Elastic modulus (E) was calculated from the initial slope of the stress-strain curve. Stress at yielding
199 (σ_y) and stress (σ_b) and elongation (ϵ_b) at break were also determined. These results are reported as the
200 average value \pm standard deviation, obtained testing six different specimens.

201 **2.8 Barrier properties**

202 Barrier capability to oxygen and carbon dioxide was evaluated by a manometric method using a
203 Permeance Testing Device, type GDP-C (Brugger Feinmechanik GmbH), according to ASTM 1434-
204 82, DIN 53 536 and ISO/DIS 15 105-1 protocol. The measurements were performed on a film surface
205 of 78.5 cm², under a gas stream of 100 cm³/min, at 23 and 38 °C, and 0 and 85 % relative humidity.
206 The results have been expressed as gas transmission rate (GTR, in cm³ cm m² d⁻¹ atm⁻¹), which defines
207 the permeability to gas of the film. The measurements were made in triplicate and the result was
208 expressed as average value \pm standard deviation.

209 **2.9 Composting tests**

210 Composting studies have been carried out at 58 °C in mature compost kindly supplied by
211 HerAmbiente S.p.A. Films of about 20x20 mm² (50 mg) were placed in a 100 mL bottle containing
212 wet compost. Specimens were withdrawn from compost in triplicate at different time intervals,
213 washed and dried over P₂O₅.

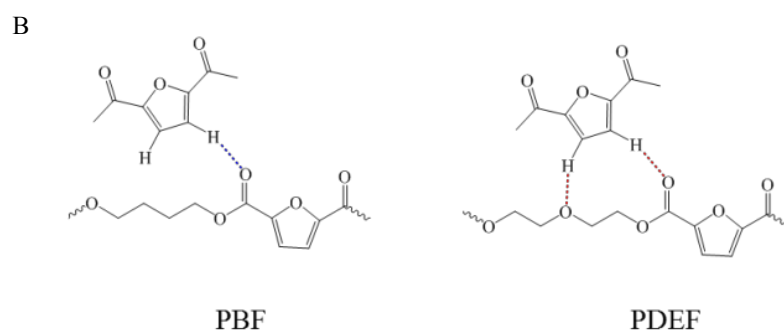
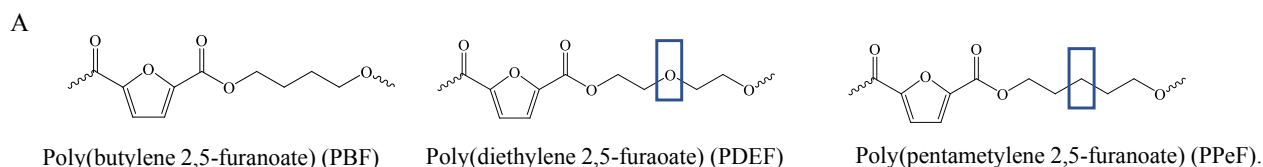
214 **2.10 SEM investigation**

215 Surface characterization was carried out by scanning electron microscopy (SEM). SEM images were
216 acquired on a desktop Phenom microscope on metal sputtered film samples glued on aluminum
217 holders with carbon tape.

218 3. Results and discussion

219 3.1 Molecular characterization

220 In **Scheme 1A**, the chemical structure of poly(diethylene 2,5-furanoate) (PDEF) is reported, together
221 with the formulas of the two homopolymers poly(butylene 2,5-furanoate) (PBF) and
222 poly(pentamethylene 2,5-furanoate) (PPEF) to which PDEF has been compared throughout the
223 present study. All the polyesters present a furan ring in the acid subunit, the difference being in the
224 glycolic moiety. In case of PBF, four methylene groups are present. PDEF has the same number of -
225 CH₂- groups, plus an ether-oxygen atom in between, this latter replaced by a methylene group in case
226 of PPEF. PDEF could be considered as derived, on one side from PBF by the insertion of a central O
227 atom in the glycol moiety and, on the other, from PPEF by the substitution of the central -CH₂- group
228 with a -O- one.



229
230 **Scheme 1. A)** Molecular structures of poly(diethylene 2,5-furanoate) (PDEF), poly(butylene 2,5-
231 furanoate) (PBF) and poly(pentamethylene 2,5-furanoate) (PPEF); **B)** Inter-chain hydrogen bonds in
232 PBF and PDEF matrices. For PPEF, a PBF-like behaviour was also supposed.

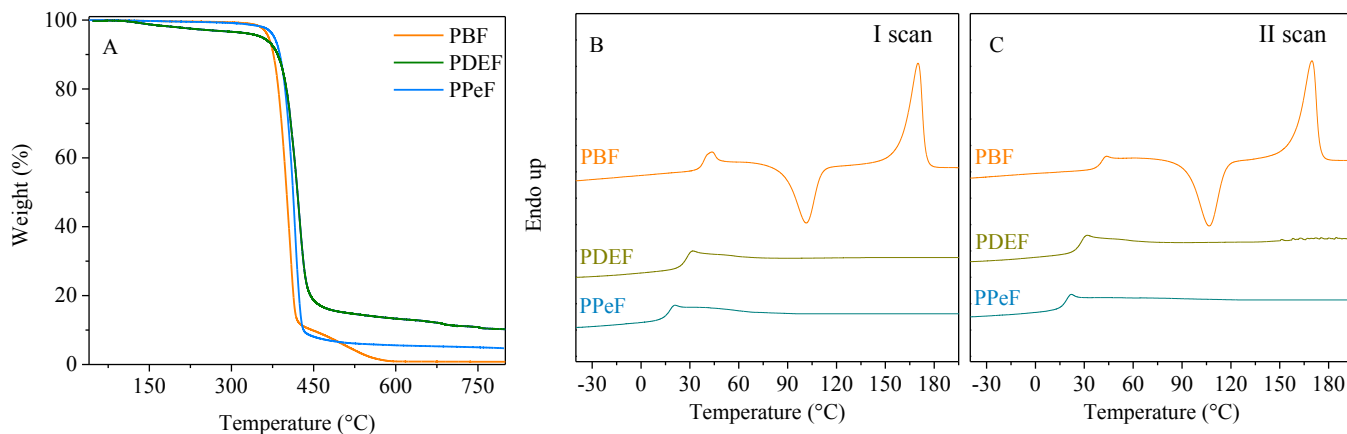
233

234 In **Fig. S1** the PDEF ¹H-NMR spectrum, together with the spectra of PBF and PPeF, is reported. As
235 one can see, the expected structure for PDEF was confirmed. In details, the -CH₂- groups of the
236 diethylene glycolic unit gave rise to two triplets at 3.82 (f) and 4.49 ppm (e), while the two d protons
237 proper of the furan ring produced a singlet (a) located at 7.20 ppm. PBF showed the same signal at
238 7.34 ppm (a), then the peaks of the b and c methylene groups of the butylene subunit could be
239 observed at 4.51 and 1.99 ppm, respectively. PPeF, beside the furan ring signal (g) at 7.20 ppm,
240 presented three different peaks due to the methylene hydrogen atoms at 4.35 (h), 1.84 (i) and 1.57
241 ppm (j). The high molecular weight, obtained by means of GPC and reported in **Table 1**, confirmed
242 the good control of the PDEF synthetic route, analogously to PBF and PPeF homopolymers.³³ The
243 polydispersity index (Đ) resulted close to 2, as expected for a polycondensation process.

244 The use of traditional Titanium-based catalysts has made possible to obtain a polymer with a
245 significantly higher molecular weight than that previously obtained by others using a lipase as
246 catalyst.⁶⁵

247 **3.2 Thermal characterization**

248 TGA analysis has been carried out to follow PDEF weight loss during heating scan under inert
249 atmosphere (nitrogen). The corresponding thermogravimetric curve is reported in **Fig. 1A**, together
250 with those previously obtained for PBF and PPeF, while the corresponding T_{max} values are listed in
251 **Table 1**. The derivative curves of thermograms are reported in **Fig. S2**. It is worth noticing the high
252 thermal stability of all the furan-based polyesters here evaluated.



253

254 **Fig. 1. A)** Thermogravimetric analysis curves of PBF, PDEF and PPeF samples obtained by heating
 255 at 10°C/min under nitrogen atmosphere; **B)** DSC traces of first heating scan of the compression
 256 moulded films and **C)** second heating scan after melt quenching (20 °C/min) of PBF, PDEF, PPeF.

257

258 In agreement with previous studies,⁶⁷⁻⁶⁹ PBF degraded at lower temperature (and comparable to the
 259 one evidenced by Kainulainen et al.⁶⁴) compared with the other two samples, reaching the maximum
 260 degradation rate at 407°C, while PDEF had the highest stability despite an initial weight loss of 4%
 261 occurring at approximately 100°C. The presence of -O- ether linkages along the macromolecular
 262 backbone, in fact, increased the tendency of the material to absorb polar molecules as water. The
 263 evaporation of the adsorbed H₂O molecules could be likely responsible for this initial weight loss
 264 step in PDEF. The highest T_{max} value obtained for PDEF could be due to the higher energy of the C-
 265 O bond, present in the diethylene glycol moieties, less prone to random scission compared with C-C
 266 bond (358 kJ/mol vs. 346 kJ/mol, respectively⁷⁰), proper of PBF and PPeF. Another important aspect
 267 was related to the formation of inter-chain hydrogen bonds, as shown in **Scheme 1B**. The
 268 establishment of inter-chain hydrogen bonds for furan-based polyesters, in addition to π-π interaction
 269 between the aromatic rings, has been evidenced by dielectric experiments, rheological analysis⁷¹ and
 270 lastly proposed through simulation studies.⁷² Considering the chemical structure, one can hypothesize
 271 that the presence of an ether-oxygen atom in the PDEF unit could increase the hydrogen bond density,
 272 thus improving the thermal resistance of the material, since the energy provided to polymer chains,

273 during heating, is first and preferentially used to break these physical links before breaking covalent
274 bonds. On the contrary, the lowest thermal stability of PBF among all the samples under study could
275 be ascribed to the lowest number of hydrogen bonds. The glassy state of PBF at room temperature
276 could limit the establishment of such inter-chain interactions, since at 25 °C, the PBF polymer chains
277 have lower molecular mobility than those of the rubbery PPeF sample.

278

279 Calorimetric analysis was performed in order to define the thermal transitions proper of the three
280 samples subjected to compression molding. The DSC traces and the relative data are reported in **Fig.**
281 **1** and in **Table 1**, respectively. The cooling scans between I and II heating scans reported in **Fig. S3**.

282 PBF film presented a melting peak centered at 164°C and preceded by a cold crystallization
283 endotherm located at 87°C; since $\Delta H_m > \Delta H_{cc}$, PBF film could be considered as semicrystalline. PDEF
284 and PPeF did not present any melting peaks, showing no capability of organizing their
285 macromolecules in crystalline structure through the compression molding process, in agreement with
286 previous studies.^{32,73} Just a glass transition step, respectively at 24 °C and 13 °C, was observed; in

287 both cases, the values recorded were lower than the PBF one. Looking at the chemical formulas of
288 **Scheme 1A**, one can see that PDEF and PPeF are characterized by longer glycolic subunits (PDEF:
289 4 -CH₂- and 1 -O-; PPeF: 5 -CH₂- moieties) compared with PBF (4 -CH₂- moieties). Even if the nature
290 of the atom changes, longer glycols favor macromolecular mobility, moving T_g towards lower
291 temperature.⁷⁴ T_{g,PDEF} can be compared with T_{g,PPeF}, due to their common fully amorphous nature. As
292 one can see, T_{g,PDEF} > T_{g,PPeF}, the difference due to the high electronegativity of heteroatoms in the
293 glycolic unit of PDEF, favouring inter chain interactions (reduced chain mobility).

294 Despite the comparable aliphatic segment length, the highly electronegative oxygen in the glycolic
295 portion of PDEF promoted inter-chain interactions (hydrogen bonds as well as Van der Waals
296 interactions). In this way, the segmental relaxation was hampered, and thus glass transition
297 temperature increased.

298

299 **Table 1.** Molecular, thermal and mechanical characterization data of PDEF, PBF and PPeF films.300 WCA ($^{\circ}$) and GTR values to oxygen and carbon dioxide at 23 $^{\circ}$ C, RH 0% are also collected.

			PBF	PDEF	PPeF
GPC		M_n [g/mol]	27300 \pm 100	21400 \pm 100	29600 \pm 100
		\bar{D}	2.3 \pm 0.1	2.3 \pm 0.1	2.4 \pm 0.1
TGA		T_{MAX} [$^{\circ}$ C]	407 \pm 1	418 \pm 1	414 \pm 1
DSC	I SCAN	T_g [$^{\circ}$ C]	39 \pm 1	24 \pm 1	13 \pm 1
		ΔC_p [J/g \cdot° C]	0.24 \pm 0.01	0.45 \pm 0.01	0.39 \pm 0.01
		T_{cc} [$^{\circ}$ C]	102 \pm 1	/	/
		ΔH_{cc} [J/g]	26 \pm 1	/	/
		T_m [$^{\circ}$ C]	170 \pm 1	/	/
		ΔH_m [J/g]	35 \pm 1	/	/
	II SCAN	T_g [$^{\circ}$ C]	39 \pm 1	24 \pm 1	13 \pm 1
		ΔC_p [J/g \cdot° C]	0.28 \pm 0.01	0.47 \pm 0.01	0.43 \pm 0.01
		T_{cc} [$^{\circ}$ C]	107 \pm 1	/	/
		ΔH_{cc} [J/g]	30 \pm 1	/	/
		T_m [$^{\circ}$ C]	170 \pm 1	/	/
		ΔH_m [J/g]	35 \pm 1	/	/
Tensile test		σ_y [MPa]	11 \pm 2	7 \pm 1	/
		σ_b [MPa]	21 \pm 3	4 \pm 0.2	6 \pm 1
		ϵ_b [%]	157 \pm 10	502 \pm 100	1050 \pm 200
		E [MPa]	1290 \pm 140	673 \pm 76	9 \pm 1
WCA		Θ [$^{\circ}$]	90 \pm 2	74 \pm 1	93 \pm 3
Barrier properties		O_2 -TR [cm ³ cm / m ² d atm]	0.10 \pm 0.006	0.0022 \pm 0.0002	0.0016 \pm 0.0001
		CO_2 -TR [cm ³ cm / m ² d atm]	0.19 \pm 0.01	0.0018 \pm 0.0001	0.0014 \pm 0.0001

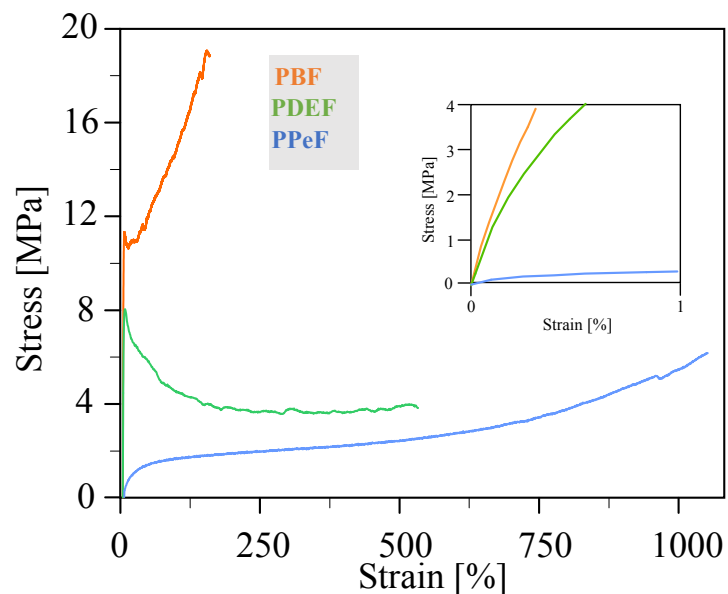
301

302

303 The three molten samples were subjected to fast cooling and analysed during a second heating
304 measurement. As expected, PDEF and PPeF resulted again completely amorphous. As concerns PBF,
305 a major polymer fraction could be quenched in the amorphous phase thanks to the high cooling rate,
306 even though no completely amorphous sample could be obtained. As evidenced by II scan DSC trace,
307 once T_g was exceeded, PBF macromolecules were able to fold in an ordered structure ($T_{cc} = 107\text{ }^\circ\text{C}$;
308 $\Delta H_{cc} = 30\text{ J/g}$) which melts at higher temperature ($T_m = 170\text{ }^\circ\text{C}$; $\Delta H_m = 35\text{ J/g}$). Despite the high cooling
309 rate, ΔH_m still keeps slightly higher than ΔH_{cc} .

310 **3.3 Mechanical characterization**

311 Stress-strain measurements were conducted on PDEF films. The obtained curve is reported in **Fig. 2**,
312 while the related data are collected in **Table 1**, together with the results previously got for PBF and
313 PPeF samples. In details, PBF film showed high elastic modulus and stress at break, and quite low
314 deformation at break in line with its semicrystalline nature, together with a T_g above room
315 temperature. Differently, thanks to its amorphous nature and a T_g below room temperature, PPeF was
316 characterized by an elastic modulus reduced by two orders of magnitude, together with an outstanding
317 elongation at break (more than 1000 %). Moreover, as previously reported,³² PPeF was able to recover
318 its initial shape thanks to a supramolecular 1-D, 2-D structure springing from inter-chain hydrogen
319 bonds established between macromolecular chains. PDEF had a mechanical behavior intermediate
320 between the one typical of a semicrystalline material, as PBF, and that of a rubbery fully amorphous
321 polymer, as PPeF. Like PBF, PDEF undergoes yielding,^{75,76} a phenomenon which was not observed
322 in PPeF. The lack of crystallites in PDEF produced a reduction of E and σ_y compared to PBF. This
323 decrement was contained by the interactions among different chains, thanks to the oxygen atom of
324 the glycolic subunit, which helped keeping the elastic modulus and the strain before yielding quite
325 high. At the same time, the higher chain mobility of PDEF with respect to PBF (lower T_g), coming
326 from the introduction of O atom, allowed reaching a 500% ϵ_b .



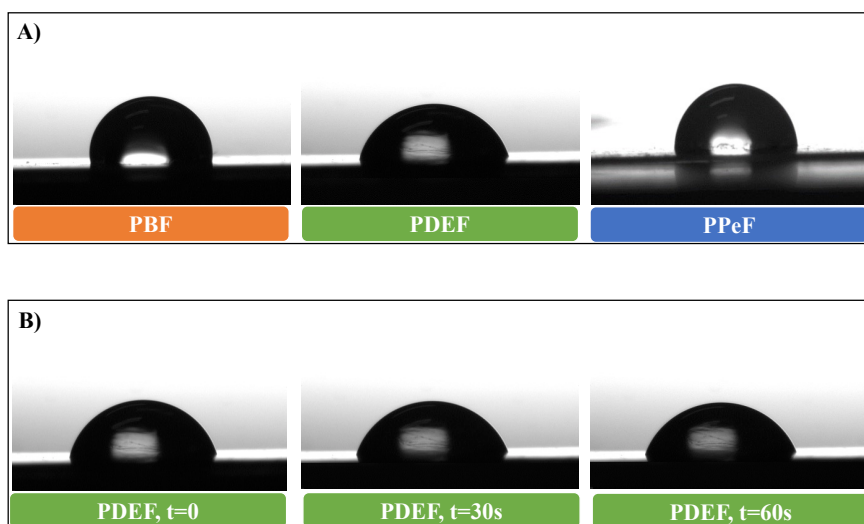
327

328 **Fig. 2.** Stress-strain curves of PBF, PDEF and PPeF films. In the inset the region corresponding to
 329 low values of stress and strain is reported.

330 3.4 Water contact angle

331 In order to evaluate the surface hydrophilicity of PDEF film, the interaction between film and water
 332 was investigated through water contact angle measurements. Particular attention was devoted to the
 333 effect of the introduction of an oxygen atom in the polymer backbone. Again, the outcomes obtained
 334 for PDEF film have been compared with the PBF and PPeF ones.

335 As it is clearly visible from **Fig. 3A** and from the data in **Table 1**, PDEF resulted the most hydrophilic
 336 film, being the WCA_{PDEF} lower than both WCA_{PBF} and WCA_{PPeF} . These results suggest that the
 337 introduction of ether-oxygen in the PBF repeating unit increases the polarity of the material, as
 338 already suggested by previous studies.⁷⁷



339

340 **Fig. 3. A)** Images of water drops deposited on PBF, PDEF and PPeF films; **B)** water drop on PDEF
 341 after 0, 30 and 60 s from deposition.

342

343 The high affinity with water was in line with the TGA results obtained for PDEF. The initial weight
 344 loss observed during the thermogravimetric analysis can be ascribed to the release of the humidity
 345 absorbed from the environment. By replacing the oxygen atom of the PDEF glycolic subunit with a
 346 non-polar $-CH_2-$ group, obtaining the PPeF chemical structure, the hydrophobic character rose again.
 347 WCA value of PPeF is similar to that of PBF, despite the greater length of the aliphatic portion (4 -
 348 CH_2- for PBF vs. 5 $-CH_2-$ for PPeF).

349 In **Fig. 3B**, the profile change of the drop deposited on PDEF film as a function of time was reported.

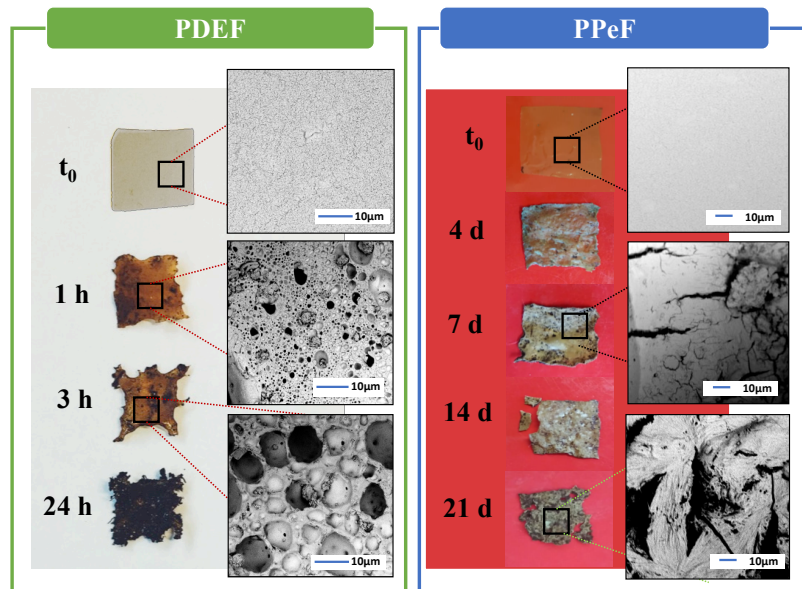
350 A clear difference in contact angle could be observed just after 30 s from the release of the water
 351 drop. A completely different behaviour was observed for PPeF and PBF, for both of which no
 352 evolution of the drop shape with time was detected. The drop shape evolution on PDEF surface is
 353 further evidence of its improved hydrophilicity with respect to PBF and PPeF.

354 **3.5 Composting test**

355 In order to evaluate the potential end-of-life destination of PDEF-based products, composting tests
 356 were conducted. For each sample, square shaped films were incubated in adequately prepared
 357 compost and maintained under controlled atmosphere (58°C, 90% relative humidity). Then, several

358 withdrawals were operated at different times (**Fig. 4**). The composting measurements were also
359 carried out on PBF and PPeF samples. As regards PBF, after 62 days in compost, no changes on the
360 film surface nor in the gravimetric weight were observed.

361



362

363 **Fig. 4.** PDEF and PPeF film images collected at different composting times: macroscopic view (left)
364 and SEM images (right).

365

366 A deeply different behaviour was observed for PDEF, which underwent degradation as soon as
367 incubated (**Fig. 4**). Just after 1 hour, the film macroscopically changed in colour and dimension, holes
368 and cracks were clearly observed with SEM. In particular, the cavities increased in size with the
369 incubation time, and after just 3 hours, the surface was almost completely covered of holes. After 24
370 hours of incubation, the film was wholly incorporated in compost. The high tendency to degrade
371 comes from the high hydrophilicity of PDEF given by the oxygen atoms inserted in the glycolic
372 subunit, and from the rubbery state of the polymer under the experimental conditions. Both these
373 features favour the diffusion of water molecules and microorganisms' attack. It is worth noting that
374 PDEF film did not undergo solubilization, as confirmed by additional experiments carried out in neat
375 water. In this case, no changes in PDEF film both at micro- and macroscopic level were observed,

376 even after months. As concerns PPeF, its degradation proceeded very fast, but at lower extent
377 compared with PDEF. Also in this case $T_{\text{incubation}} > T_{g,\text{PPeF}}$, but degradation was slowed down likely
378 because of the lower hydrophilicity. Anyway, after 4 days, macroscopical changing on the film
379 surface could be seen and, after 7 days, cracks and holes could be observed microscopically via SEM
380 analysis. In 21 days, the film was deeply compromised by degradation process both at micro- and
381 macroscopic level (**Fig. 4**). Given the compost contamination of the incubated PDEF and PPeF films,
382 it was not possible to perform weight loss measurements.

383 The huge slowing down of composting rate for PBF films has to be ascribed to its semicrystalline
384 nature and lower macromolecular mobility ($T_{g,\text{PBF}} > T_{g,\text{PDEF}}, T_{g,\text{PPeF}}$) more than to its quite high
385 hydrophobicity, being this last comparable to PPeF one ($\text{WCA}_{\text{PBF}} \approx \text{WCA}_{\text{PPeF}}$).

386 **3.6 Barrier properties**

387 Barrier properties are influenced by several factors that can have different impact on the final
388 performance. As a general trend, all factors that increase free volume among chains worsen barrier
389 properties. A pertinent example is the macromolecule flexibility, which is related to the glass
390 transition temperature. In particular, the lower the T_g the higher the number of unoccupied spaces,
391 which cause the increase of gas transmission rate (GTR). Differently, the presence of ordered phases
392 hampers the passage of gases through the film. In addition to the three-dimensional crystals, in the
393 systems containing aromatic or aliphatic rings connected by flexile moieties, 1D- and 2D-ordered
394 phases can develop, arising from Van der Waals forces, π - π stacking and polar interactions.⁷⁸⁻⁸²
395 Barrier properties also depend on the possibility of ring flipping,⁸³ and of macromolecular
396 arrangements, which may affect the overall dipolar moment without changing the chemistry.⁸⁴ In
397 addition to them, in the case of furan-based polymers, the establishment of hydrogen bonds can be
398 also considered.^{32,33,71,72} PDEF gas barrier properties were analysed and compared with those of PBF
399 and PPeF.

400 The permeability performances to two different pure gases, O_2 and CO_2 , were evaluated on the
401 compression moulded films. In **Fig. 5A** the results, expressed as gas transmission rate (GTR), were

402 reported. The experiments were conducted sequentially, as follows: i) temperature (T) 23°C, relative
403 humidity (RH) 0%; ii) T 23°C, RH 85%; iii) T 23°C, RH 0%. From the first test conducted at 23°C
404 in dry atmosphere, it was clear that PBF presented the highest values of GTR among the series, despite
405 its higher glass transition temperature and semicrystalline nature. Differently, PDEF and PPeF, even
406 though amorphous and with T_g values around the temperature of measuring, resulted very outstanding
407 and with comparable performance. An explanation could be found, as mentioned before, in the
408 presence of a particular macromolecular arrangement that blocked the passage of gases through the
409 materials.⁸⁵ In the case of PPeF, as previously reported,^{32,33} 1-D, 2D-ordered domains developed
410 during compression moulding with consequent improvement of gas barrier performance. This
411 peculiar microstructure originated from inter-chain hydrogen bonds, these last also present, and to
412 greater extent, in PDEF. The presence of ether-oxygen atom in PDEF repeating unit enhanced the
413 number of hydrogen bonds favouring the inter-molecular forces. These last lead to a compact array,
414 that hampered the gas molecules passage. At the same time, the insertion of an oxygen atom into the
415 glycol subunit decreases the symmetry of the aliphatic segment, reducing the macromolecular sorting.
416 In other words, the density of the inter-chain hydrogen bond increases due to the presence of ether O
417 atoms, but their random distribution determines a not enough long chain arrangement, not detectable
418 through diffractometric measurements. Nevertheless, unexpectedly, the barrier performances of the
419 PDEF were not superior to those of PPeF. The result could be explained considering that the
420 formation of the compact array is somewhat contrasted by the lower mobility of the PDEF
421 macromolecular chains compared to those of the PPeF ($T_{g,PDEF} > T_{g,PPeF}$).
422 Afterwards, the three films were subjected to permeability tests at 85% RH, keeping the temperature
423 constant at 23°C. In case of PBF, an improvement of barrier performance was observed, while for
424 PDEF, permeability values remained almost constant. The result was quite surprising considering the
425 usually observed plasticizing effect of water, which, enhancing the chain mobility, determined an
426 increment of the free volume. On the other side, the same plasticizing effect detected for PPeF, caused
427 a slight increase of GTR values under humid conditions. To explain the behaviour of PDEF and PBF

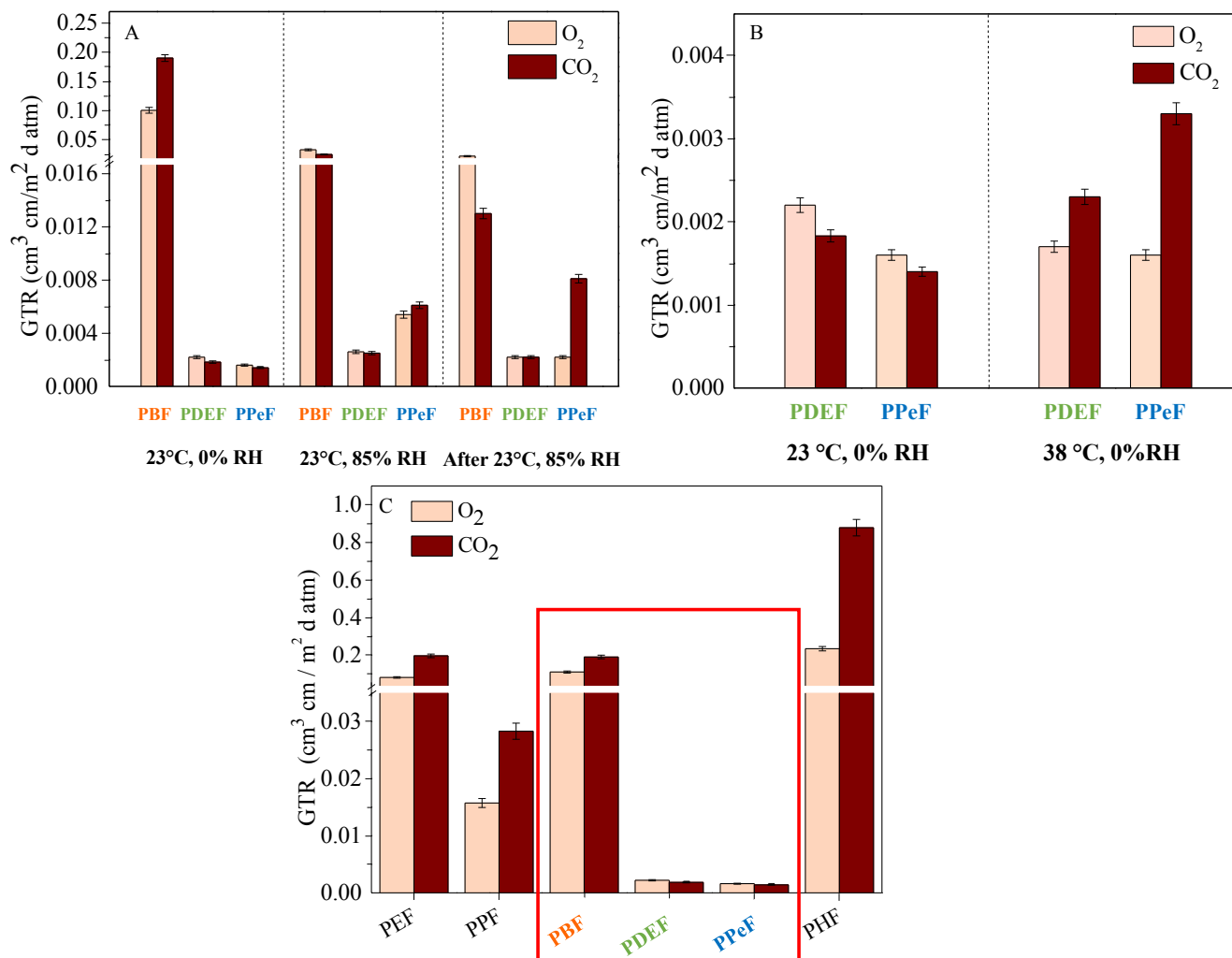
428 films, it was supposed that water enhanced the inter-chain interactions occupying the empty sites at
429 the oxygen atoms of the furan ring and, in case of PDEF, also at the oxygen of the glycolic subunit.
430 Hence, a more compact and dense new structure was formed, responsible for the decreasing of the
431 GTR values.⁸⁵ In the case of PPeF, also containing furan O atoms in the furan ring, the longer glycolic
432 part compared to PBF decreased the density of furan ring per unit length. Therefore, the plasticizing
433 effect of water prevailed on the formation of a more compact microstructure arising from the
434 hydrogen bonds establishment. In PDEF, characterized by repeating unit length comparable to PPeF,
435 the presence of the oxygen atom instead of the central methylene group explained the different
436 behaviour in wet environment.

437 In the third experiment, the films were firstly subjected to vacuum in order to remove the moisture
438 residues and then, a new test was performed at 23°C and 0% RH. PBF and PDEF maintained the
439 same good performances reached under humid conditions. It is plausible that the vacuum applied was
440 not affecting the hydrogen bonds formed among water and furan/ether oxygen. For PPeF, it could be
441 hypothesized that the free molecules of water trapped inside the material and acting as plasticizer,
442 were removed by vacuum. Conversely, those forming hydrogen bonds with the furan ring remained
443 inside the material, making GTR-O₂ value decrease and GTR-CO₂ one almost unvaried.

444 Another aspect to consider was the different perm-selectivity ratio, defined as GTR_{CO_2}/GTR_{O_2} , which
445 is an indication of the different barrier performance towards the two gases. It should be remembered
446 that oxygen is a small and non-polar molecule characterized by a transmission rate lower than that of
447 the larger carbon dioxide, which contains polar C-O covalent bonds.⁵⁰ Consequently, the perm-
448 selectivity ratio is usually higher than 1. Usually, in polyesters $GTR_{CO_2} > GTR_{O_2}$, meaning carbon
449 dioxide passed through the films easier than O₂. In the furan-based polyesters, a peculiar behaviour
450 with particularly low GTR values for CO₂ had been documented.^{32,86-88} This evidence was ascribed
451 to the presence of permanent dipoles in CO₂ interacting with the polar groups of polymeric chains

452 (furan ring), thus increasing CO₂ solubility and simultaneously decreasing its diffusivity. The
 453 consequent result is a GTR_{CO₂}/GTR_{O₂} ratio close to 1 for furan-containing polyesters.

454



455

456 **Fig. 5. A)** GTR-O₂ and -CO₂ of PBF, PDEF and PPeF, for three subsequent experiments conducted
 457 at 23°C in different conditions of humidity; **B)** GTR-O₂ and -CO₂ of PDEF and PPeF at 23 and 38
 458 °C; **C)** GTR-O₂ and -CO₂ of different furan-based polyesters (PEF³⁴, PPF¹⁰, PHF¹⁰).

459

460

461 Considering the three-step experiment reported in **Fig. 5A**, a different effect of humidity conditions
 462 on perm-selectivity ratio could be found for PBF, PDEF and PPeF films.

463 As concerns PBF, in the first test conducted, the driving force was the dimension of the molecules.
464 Operating at 85% RH, new polar interactions between water molecules and polymer chains formed,
465 favouring CO₂ solubility. The effect kept constant even returning to dry environment.
466 In case of PDEF, its higher polarity due to the O atom insertion in the PBF backbone, helped to
467 maintain the GTR_{CO_2}/GTR_{O_2} ratio always close to 1. As regards PPeF, the trend observed was
468 different: humidity determined an increment of perm-selectivity ratio, which further increased after
469 removing free water molecules by vacuum. This trend could be explained considering that H₂O first
470 acted as plasticizer, enhancing polymer chain mobility, and then left vacancies after vacuum was
471 applied. Both these effects increased the free volume, favouring mainly the passage of the fastest CO₂
472 molecules. These last, in turn, were less soluble in PPeF than in PBF and especially in PDEF films.
473 PDEF and PPeF were also tested at 38°C to simulate hot weather conditions. As one can see from
474 **Fig. 5B**, despite at this temperature macromolecular chains of both polymers were in a complete
475 mobile state, barrier properties did not suffer a general worsening. This experiment supports, one
476 more time, the hypothesis of supramolecular arrays originated from hydrogen bonds among the
477 chains. As evident, these compact structures were not affected by the increasing of temperature, since
478 the polymers maintain their performances. Differently, the increase of temperature in case of common
479 polyesters leads to higher free volume among the macromolecules, favouring gas permeation.
480 Anyway, an increase of CO₂ gas transmission rate was detected by increasing temperature. As already
481 mentioned, the gas passage depended on both solubility and diffusivity. This latter generally rises
482 with temperature, the effect being more intense for the gas molecules characterized by the most
483 chaotic motions, such as CO₂ molecules. In both cases, the performances to O₂ at 23°C and 38°C
484 were constant, while GTR_{CO_2} values increased.
485 In **Fig. 5C**, a comparison of PDEF with PBF, PPeF and other furan-based polyesters was reported.
486 As one can see, PDEF and PPeF had GTR values much lower than the other materials.

487 In addition, an odd/even effect could be observed: the materials with odd number of -CH₂- groups
488 resulted more performant compared to the even numbered -CH₂- containing ones. Surprisingly, PDEF
489 and PPeF presented GTR values lower than those of PPF, despite their lower T_g (T_{g,PPeF} = 13°C;
490 T_{g,PDEF} = 24°C; T_{g,PPF} = 52°C). As previously reported, the deviating behaviour of PPeF and PDEF
491 could be attributed to the supramolecular compact phase coming from the hydrogen bond formation,
492 this last being favoured in rubbery amorphous furan-polyesters as PDEF and PPeF.
493 As regards the materials containing an even number of -CH₂- groups, PEF, PBF and PHF, a
494 progressive worsening of gas barrier performances can be observed, ascribable to different reasons
495 as previously reported:^{33,89} (i) increasing amount of the so called disclinations; (ii) increasing fraction
496 of 3D-ordered phase at the expense of the more performant 2D-one; (iii) increasing of free volume
497 fraction (T_{g,PEF} > T_{g,PBF} > T_{g,PHF}).

498 **4. Conclusions**

499 The use of traditional synthetic Ti-based catalysts together with an optimized solvent-free two-stage
500 polycondensation process permitted to obtain a 100% bio-based high molecular weight
501 poly(diethylene 2,5-furanoate) (PDEF). The polymer could be processed in form of thin freestanding
502 films by compression moulding, although completely amorphous and with a T_g around room
503 temperature. A similar behaviour was previously observed for poly(pentamethylene 2,5-furanoate)
504 (PPeF), with respect to which the polymer object of this study has some important similarities in
505 terms of properties. In particular, both polyesters are characterized by very high thermal stability
506 (PDEF's one even slightly higher than that of PPeF), exceptional gas barrier properties both at room
507 temperature and at 38°C, preserved in the presence of humidity. Lastly, they are both compostable,
508 although PDEF degrades much faster than PPeF, mainly due to its greater hydrophilicity. In terms of
509 mechanical response, a fundamental property for a possible application in food packaging, PDEF
510 showed an intermediate behaviour between poly(butylene 2,5-furanoate) (PBF) and PPeF. In fact,
511 PDEF film exhibited the flexibility typical of PPeF, even though not an elastomeric behaviour (PDEF

512 stress-strain curve shows yielding), but a much higher elastic modulus and stress at break as PBF,
513 which confer to the material toughness and ductility. Therefore, with PDEF both the mechanical
514 limits of PBF (brittleness) and of PPeF (too high softness) are overcome, without compromising the
515 outstanding thermal stability, gas barrier properties and compostability of PPeF. The goal was
516 achieved through a small chemical modification of polymer chemical structure, i.e. the insertion of
517 an ether oxygen atom into the glycol subunit, centrally positioned. As known from basic chemistry,
518 oxygen is characterized by high electronegativity and small dimensions, and these characteristics
519 have had a significant impact on the final properties of the polymer. Specifically:

- 520 - The lower dimension of oxygen with respect to carbon atom affected the chain constitutional
521 regularity with consequent suppression of the polymer crystallization capacity (PDEF is
522 amorphous, whereas PBF is semicrystalline). Moreover, C-O bond is shorter than C-C one,
523 implying for ethereal bond a higher energy (PDEF is more thermally stable than PBF); the
524 insertion of an oxygen atom in glycol subunit also makes its polymer chain more flexible than
525 that of PBF, the aliphatic part being longer;
- 526 - The high oxygen electronegativity strengthens inter-chain interactions (hydrogen bonds
527 involving furan ring and Van der Waals interactions) responsible of the outstanding gas
528 barrier (similar to those of PPeF) and mechanical properties (better than those of both PBF
529 and PPeF) and increases polymer hydrophilicity, the parameter determining the very fast
530 compostability of this polyester.

531 In conclusion, PDEF represents a very promising candidate to obtain an easily recyclable mono-
532 material package and also for producing single-use plastic packaging compostable in just one day.

533

534 **Author contributions**

535 S.Q. M.S. synthesized and characterized the polymer. V.S. performed gas barrier measurements.
536 S.Q., G.G., M.S. and N.L. analyzed the overall experimental data. M.S. and N.L. wrote manuscript.
537 G.G., M.S. and N. L. corrected and reviewed the manuscript. N.L. supervised and financed the work.

538 **Conflicts of interest**

539 The authors declare no conflict of interests.

540 **Acknowledgments**

541 S.Q, G.G., M.S., N.L., and V.S. acknowledge the Italian Ministry of University and Research. This
542 publication is based upon work from COST Action FUR4Sustain, CA18220, supported by COST
543 (European Cooperation in Science and Technology).

544 The authors thank Dr. Massimo Gazzano for his cooperation in the acquisition of SEM micrographs.

545 **Supplementary data**

546 These files can be found in the supplementary data:

547 Fig. S1. ¹H-NMR spectra of PBF, PDEF and PPeF (from the top to the bottom) with the relative peak
548 assignment.

549

550 **References**

- 551 1. Plastics - The facts 2020. *PlasticsEurope*, 2020,
552 <https://www.plasticseurope.org/en/resources/publications/4312-plastics-facts-2020> (accessed
553 [July 2021](#)).
- 554 2. <https://www.statista.com/statistics/664906/plastics-production-volume-forecast-worldwide/>
555 [STATISTA 2021](#) (accessed [September 2021](#)).
- 556 3. Plastic Market Size, Share & Trends Analysis Report by Product (PE, PP, PU, PVC, PET,
557 Polystyrene, ABS, PBT, PPO, Epoxy Polymers, LCP, PC, Polyamide), by Application, by

- 558 End-use, by Region, and Segment Forecasts, 2021 – 2028, Grand view Research 2021
559 (accessed: September 2021).
- 560 4. RameshKumar, S.; Shaiju, P.; O'Connor, K. E.; P, R. B. Bio-Based and Biodegradable
561 Polymers - State-of-the-Art, Challenges and Emerging Trends. *Curr. Opin. Green Sustain.*
562 *Chem.* **2020**, *21*, 75–81.
- 563 5. Mülhaupt, R. Green Polymer Chemistry and Bio-based Plastics: Dreams and Reality.
564 *Macromol. Chem. Phys.* **2013**, *214*, 159–174.
- 565 6. Rabnawaz, M.; Wyman, I.; Auras, R.; Cheng, S. A roadmap towards green packaging: the
566 current status and future outlook for polyesters in the packaging industry. *Green Chem.* **2017**,
567 *19*, 4737-4753.
- 568 7. Álvarez-Chávez, C. R.; Edwards, S.; Moure-Eraso, R; Geiser, K. Sustainability of bio-based
569 plastics: General comparative analysis and recommendations for improvement. *J. Clean Prod.*
570 **2012**, *23*, 47–56.
- 571 8. Papageorgiou, G. Z. Thinking Green: Sustainable Polymers from Renewable Resources.
572 *Polymers* **2018**, *10*, 952.
- 573 9. Zhang, Q.; Song, M.; Xu, Y.; Wang, W.; Wang, Z.; Zhang, L. Bio-based polyesters: Recent
574 progress and future prospects. *Prog. Polym. Sci.* **2021**, *120*, 101430.
- 575 10. Morris, A. B. *The Science and Technology of Flexible Packaging. Multilayer Films from*
576 *Resin and Process to End Use*, Elsevier, **2016**.
- 577 11. Reichert, C. L.; Bugnicourt, E.; Coltelli, M.-B.; Cinelli, P.; Lazzeri, A.; Canesi, I.; Braca, F.;
578 Martínez, B. M.; Alonso, R.; Agostinis, L.; Verstichel, S.; Six, L.; De Mets, S.; Gómez, E. C.;
579 Ißbrücker, C.; Geerinck, R.; Nettleton, D. F.; Campos, I.; Sauter, E.; Pieczyk, P.; Schmid, M.
580 Bio-Based Packaging: Materials, Modifications, Industrial Applications and Sustainability.
581 *Polymers* **2020**, *12*, 1558.
- 582 12. Young, E.; Mirosa, M.; Bremer, P. A Systematic Review of Consumer Perceptions of Smart
583 Packaging Technologies for Food. *Front. Sustain. Food Syst.* **2020**, *4*, 63.

- 584 13. Majid, I.; Nayik, G. A.; Dar, S. M.; Nanda, V. Novel food packaging technologies:
585 Innovations and future prospective. *J. Saudi Soc. Agric. Sci.* **2018**, *17*, 454-462.
- 586 14. Bhargava, N.; Sharanagat, V. S.; S Mor, R.; Kumar, K. Active and intelligent biodegradable
587 packaging films using food and food waste-derived bioactive compounds: A review. *Trends*
588 *Food Sci. Technol.* **2020**, *105*, 385-401.
- 589 15. Firouz, M. S.; Mohi-Alden, K.; Omid, M. A critical review on intelligent and active packaging
590 in the food industry: Research and development. *Food Res. Int.* **2021**, *141*, 110113.
- 591 16. Singh, G.; Singh, S.; Kumar, B.; Gaikwad, K. K. Active barrier chitosan films containing
592 gallic acid based oxygen scavenger. *J. Food Meas. Charact.* **2021**, *15*, 585–593.
- 593 17. <https://perfectpackaging.org> (accessed: September 2021).
- 594 18. <https://www.flexpack-europe.org> (accessed: September 2021).
- 595 19. Vilela, C.; Sousa, A. F.; Fonseca, A. C.; Serra, A. C.; Coelho, J. F. J.; Freire, C. S. R.;
596 Silvestre, A. J. D. The quest for sustainable polyesters – insights into the future. *Polym. Chem.*
597 **2014**, *5*, 3119-3141.
- 598 20. Hwang, K. R.; Jeon, W.; Lee, S. Y.; Kim, M. S.; Park, Y. K. Sustainable bioplastics: Recent
599 progress in the production of bio-building blocks for the bio-based next-generation polymer
600 PEF. *Chem. Eng. J.* **2020**, *390*, 124636.
- 601 21. Sousa, A. F.; Vilela, C.; Fonseca, A. C.; Matos, M.; Freire, C. S. R.; Gruter, G. J. M.; Coelho,
602 J. F. J.; Silvestre, A. J. D. Biobased polyesters and other polymers from 2,5-furandicarboxylic
603 acid: a tribute to furan excellency. *Polym. Chem.* **2015**, *6*, 5961-5983.
- 604 22. Papageorgiou, G. Z.; Papageorgiou, D. G.; Terzopoulou, Z.; Bikiaris, D. N. Production of bio-
605 based 2,5-furan dicarboxylate polyesters: Recent progress and critical aspects in their
606 synthesis and thermal properties. *Eur. Polym. J.* **2016**, *83*, 202-229.
- 607 23. Loos, K.; Zhang, R.; Pereira, I.; Agostinho, B.; Hu, H.; Maniar, D.; Sbirrazzuoli, N.; Silvestre,
608 A. J. D.; Guigo, N.; Sousa, A. F. A Perspective on PEF Synthesis, Properties, and End-Life.
609 *Front. Chem.* **2020**, *8*, 585.

- 610 24. Terzopoulou, Z.; Papadopoulos, L.; Zamboulis, A.; Papageorgiou, D. G.; Papageorgiou, G.
611 Z.; Bikiaris, D. N. Tuning the Properties of Furandicarboxylic Acid-Based Polyesters with
612 Copolymerization: A Review. *Polymers* **2020**, *12*, 1209.
- 613 25. Iglesias, J.; Martínez-Salazar, I.; Maireles-Torres, P.; Martín Alonso, D.; Mariscal, R; López
614 Granados, M. Advances in catalytic routes for the production of carboxylic acids from
615 biomass: a step forward for sustainable polymers. *Chem. Soc. Rev.* **2020**, *49*, 5704-5771.
- 616 26. Chen, C.; Wang, L.; Zhu, B.; Zhou, Z.; El-Hout, S. I.; Yang, J.; Zhang, J. 2,5-
617 Furandicarboxylic acid production via catalytic oxidation of 5-hydroxymethylfurfural:
618 Catalysts, processes and reaction mechanism. *J. Energy Chem.* **2021**, *54*, 528-554.
- 619 27. Wojcieszak, R.; Itabaiana, I. Engineering the future: Perspectives in the 2,5-furandicarboxylic
620 acid synthesis. *Catal. Today* **2020**, *354*, 211-217.
- 621 28. Dedes, G.; Karnaouri, A.; Topakas, E. Novel Routes in Transformation of Lignocellulosic
622 Biomass to Furan Platform Chemicals: From Pretreatment to Enzyme Catalysis. *Catalysts*
623 **2020**, *10*, 743.
- 624 29. Wu, S.; Liu, Q.; Tan, H.; Zhang, F.; Yin, H. A Novel 2,5-Furandicarboxylic Acid Biosynthesis
625 Route from Biomass-Derived 5-Hydroxymethylfurfural Based on the Consecutive Enzyme
626 Reactions. *Appl. Biochem. Biotechnol.* **2020**, *191*, 1470–1482.
- 627 30. Naim, W.; Schade, O. R.; Saraci, E.; Wust, D.; Kruse, A.; Grundwaldt, J. D. Toward an
628 Intensified Process of Biomass-Derived Monomers: The Influence of 5-
629 (Hydroxymethyl)furfural Byproducts on the Gold-Catalyzed Synthesis of 2,5-
630 Furandicarboxylic Acid. *ACS Sustainable Chem. Eng.* **2020**, *8*, 11512–11521.
- 631 31. Deshan, A. D. K.; Atanda, L.; Moghaddam, L.; Rackemann, D. W.; Beltramini, J.; Doherty,
632 W. O. S. Heterogeneous Catalytic Conversion of Sugars Into 2,5-Furandicarboxylic Acid.
633 *Front. Chem.* **2020**, *8*, 659.
- 634 32. Guidotti, G.; Soccio, M.; García-Gutiérrez, M. C.; Gutiérrez-Fernández, E.; Ezquerra, T. A.;
635 Siracusa, V.; Munari, A.; Lotti, N. Evidence of a 2D-Ordered Structure in Biobased

- 636 Poly(pentamethylene furanoate) Responsible for Its Outstanding Barrier and Mechanical
637 Properties. *ACS Sustainable Chem. Eng.* **2019**, *7*, 17863–17871.
- 638 33. Guidotti, G.; Soccio, M.; García-Gutiérrez, M. C.; Ezquerra, T.; Siracusa, V.; Gutiérrez-
639 Fernández, E.; Munari, A.; Lotti, N. Fully Biobased Superpolymers of 2,5-Furandicarboxylic
640 Acid with Different Functional Properties: From Rigid to Flexible, High Performant
641 Packaging Materials. *ACS Sustainable Chem. Eng.* **2020**, *8*, 9558–9568.
- 642 34. Benson, N. U.; Bassey D. E.; Palanisami, T. COVID pollution: impact of COVID-19
643 pandemic on global plastic waste footprint. *Heliyon* **2021**, *7*, e06343.
- 644 35. Klemeš, J. J.; Van Fan, Y.; Tan, R. R.; Jiang, P. Minimising the present and future plastic
645 waste, energy and environmental footprints related to COVID-19. *Renewable Sustainable*
646 *Energy Rev.* **2020**, *127*, 109883.
- 647 36. Khoo, K. S.; Ho, L. Y.; Lim, H. R.; Leong, H. Y.; Chew, K. W. Plastic waste associated with
648 the COVID-19 pandemic: Crisis or opportunity? *J. Hazard. Mater.* **2021**, *417*, 126108.
- 649 37. Pellis, A.; Haernvall, K.; Pichler, C. M.; Ghazaryan, G.; Breinbauer, R.; Guebitz, G. M.
650 Enzymatic hydrolysis of poly(ethylene furanoate). *J. Biotechnol.* **2016**, *235*, 47-53.
- 651 38. Gigli, M.; Quartinello, F.; Soccio, M.; Pellis, A.; Lotti, N.; Guebitz, G. M.; Licoccia, S.;
652 Munari, A. Enzymatic hydrolysis of poly(1,4-butylene 2,5-thiophenedicarboxylate) (PBTF)
653 and poly(1,4-butylene 2,5-furandicarboxylate) (PBF) films: A comparison of mechanisms.
654 *Environ. Int.* **2019**, *130*, 104852.
- 655 39. Okada, M.; Tachikawa, K.; Aoi, K. Biodegradable polymers based on renewable resources.
656 II. Synthesis and biodegradability of polyesters containing furan rings. *J. Polym. Sci., Part A:*
657 *Polym. Chem.* **1997**, *35*, 2729–2737.
- 658 40. Muller, R. J.; Kleeberg, I.; Deckwer, W. D. Biodegradation of polyesters containing aromatic
659 constituents. *J. Biotechnol.* **2001**, *86*, 87–95.

- 660 41. Soccio, M.; Costa, M.; Lotti, N.; Gazzano, M.; Siracusa, V.; Salatelli, E.; Manaresi, P.;
661 Munari, A. Novel fully biobased poly(butylene 2,5-furanoate/diglycolate) copolymers
662 containing ether linkages: Structure-property relationships. *Eur. Polym. J.* **2016**, *81*, 397–412.
- 663 42. Guidotti, G.; Soccio, M.; Lotti, N.; Siracusa, V.; Gazzano, M.; Munari, A. New multi-block
664 copolyester of 2,5-furandicarboxylic acid containing PEG-like sequences to form flexible and
665 degradable films for sustainable packaging. *Polym. Degrad. Stab.* **2019**, *169*, 108963.
- 666 43. Cowie, J. M. G.; Arrighi, V. *Polymers Chemistry and Physics of Modern Materials*, 3rd
667 Edition, CRC Press, **2007**, Chapter 15.
- 668 44. Pouloupoulou, N.; Smyrnioti, D.; Nikolaidis, G. N.; Tsitsimaka, I.; Christodoulou, E.; Bikiaris,
669 D. N.; Charitopoulou, M. A.; Achilias, D. S.; Kapnisti, M.; Papageorgiou, G. Z. Sustainable
670 Plastics from Biomass: Blends of Polyesters Based on 2,5-Furandicarboxylic Acid. *Polymers*
671 **2020**, *12*, 225.
- 672 45. Thiyagarajan, S.; Vogelzang, W.; Knoop, R. J. I.; Frissen, A. E.; van Haveren, J.; van Es, D.
673 S. Biobased furandicarboxylic acids (FDCAs): effects of isomeric substitution on polyester
674 synthesis and properties. *Green Chem.* **2014**, *16*, 1957-1966.
- 675 46. Soccio, M.; Nogales, A.; García-Gutiérrez, M.; Lotti, N.; Munari, A.; Ezquerra, T. Origin of
676 the subglass dynamics in aromatic polyesters by labeling the dielectric relaxation with ethero
677 atoms. *Macromolecules* **2008**, *41*, 2651–2655.
- 678 47. Bianchi, E.; Soccio, M.; Siracusa, V.; Gazzano, M.; Thiyagarajan, S.; Lotti, N. Poly(butylene
679 2,4-furanoate), an Added Member to the Class of Smart Furan-Based Polyesters for
680 Sustainable Packaging: Structural Isomerism as a Key to Tune the Final Properties. *ACS*
681 *Sustainable Chem. Eng.* **2021**, *9*, 11937–11949.
- 682 48. Thiyagarajan, S.; Meijlink, M. A.; Bourdet, A.; Vogelzang, W.; Knoop, R. J. I.; Esposito, A.;
683 Dargent, E.; van Es, D. S.; van Haveren, J. Synthesis and Thermal Properties of Bio-Based
684 Copolyesters from the Mixtures of 2,5- and 2,4-Furandicarboxylic Acid with Different Diols.
685 *ACS Sustainable Chem. Eng.* **2019**, *7*, 18505–18516.

- 686 49. Nolasco, M. M.; Araujo, C. F.; Thiyagarajan, S.; Rudić, S.; Vaz, P. D.; Silvestre, A. J. D.;
687 Ribeiro-Claro, P. J. A.; Sousa, A. F. Asymmetric Monomer, Amorphous Polymer? Structure–
688 Property Relationships in 2,4-FDCA and 2,4-PEF. *Macromolecules* **2020**, *53*, 1380–1387.
- 689 50. Robertson, G. L. *Food Packaging Principles and Practice*, 3rd Edition, CRC Press, **2013**,
690 Chapter 2-4.
- 691 51. Davidson, M. G.; Elgie, S.; Parsons, S.; Young, T. J. Production of HMF, FDCA and their
692 derived products: a review of life cycle assessment (LCA) and techno-economic analysis
693 (TEA) studies. *Green Chem.* **2021**, *23*, 3154-3171.
- 694 52. Bozell, J. J.; Petersen, G. R. Technology development for the production of biobased products
695 from biorefinery carbohydrates—the US Department of Energy’s “Top 10” revisited. *Green*
696 *Chem.* **2010**, *12*, 539-554.
- 697 53. Bio-Based Chemicals A 2020 Update, IEA Bioenergy, available online:
698 [https://www.ieabioenergy.com/wp-content/uploads/2020/02/Bio-based-chemicals-a-2020-](https://www.ieabioenergy.com/wp-content/uploads/2020/02/Bio-based-chemicals-a-2020-update-final-200213.pdf)
699 [update-final-200213.pdf](https://www.ieabioenergy.com/wp-content/uploads/2020/02/Bio-based-chemicals-a-2020-update-final-200213.pdf) (accessed September 2021).
- 700 54. Zheng, M.; Li, X. Y.; Guan, R. Q.; Liu, Y. M.; Zhao, Y. J.; Tai, Y. L. Ionic Liquid-Catalyzed
701 Synthesis of Diethylene Glycol. *Adv. Mat. Res.* **2012**, *549*, 287-291.
- 702 55. Bioplastics market data, European-bioplastics.org (accessed September 2021).
- 703 56. Soccio, M.; Lotti, N.; Finelli, L.; Gazzano, M.; Munari, A. Influence of transesterification
704 reactions on the miscibility and thermal properties of poly(butylene/diethylene succinate)
705 copolymers. *Eur. Polym. J.* **2008**, *44*, 1722-1732.
- 706 57. Soccio, M.; Lotti, N.; Gigli, M.; Finelli, L.; Gazzano, M.; Munari, A. Reactive blending of
707 poly(butylene succinate) and poly(triethylene succinate): characterization of the copolymers
708 obtained. *Polym. Int.* **2012**, *61*, 1163-1169.
- 709 58. Fabbri, M.; Gigli, M.; Gamberini, R.; Lotti, N.; Gazzano, M.; Rimini, B.; Munari, A.
710 Hydrolysable PBS-based poly(ester urethane)s thermoplastic elastomers. *Polym. Degrad.*
711 *Stab.* **2014**, *108*, 223-231.

- 712 59. Lotti, N.; Finelli, L.; Fiorini, M.; Righetti, M. C.; Munari, A. Synthesis and characterization
713 of poly(butylene terephthalate-co-diethylene terephthalate) copolyesters. *Polymer* **2000**, *41*,
714 5297-5304.
- 715 60. Lotti, N.; Finelli, L.; Fiorini, M.; Righetti, M. C.; Munari, A. Synthesis and characterization
716 of poly(butylene terephthalate-co-triethylene terephthalate) copolyesters. *J. Appl. Polym. Sci.*
717 **2001**, *81*, 981-990.
- 718 61. Gigli, M.; Lotti, N.; Gazzano, M.; Finelli, L.; Munari, A. Novel eco-friendly random
719 copolyesters of poly(butylene succinate) containing ether-linkages. *React. Funct. Polym.*
720 **2012**, *72*, 303-310.
- 721 62. Gigli, M.; Lotti, N.; Gazzano, M.; Siracusa, V.; Finelli, L.; Munari, A.; Dalla Rosa, M. Fully
722 aliphatic copolyesters based on poly(butylene 1,4-cyclohexanedicarboxylate) with promising
723 mechanical and barrier properties for food packaging applications. *Ind. Eng. Chem. Res.* **2013**,
724 *52*, 12876–12886.
- 725 63. Gigli, M.; Lotti, N.; Gazzano, M.; Siracusa, V.; Finelli, L.; Munari, A.; Dalla Rosa, M.
726 Biodegradable aliphatic copolyesters containing PEG-like sequences for sustainable food
727 packaging applications. *Polym. Degrad. Stab.* **2014**, *105*, 96-106.
- 728 64. Kainulainen, T. P.; Hukka, T. I.; Ozeren, H. D.; Sirvio, J. A.; Hedenqvist, M. S.; Heiskanen,
729 J. P. Utilizing Furfural-Based Bifuran Diester as Monomer and Comonomer for High-
730 Performance Bioplastics: Properties of Poly(butylene furanoate), Poly(butylene bifuranoate),
731 and Their Copolyesters. *Biomacromolecules* **2020**, *21*, 743–752.
- 732 65. Jiang, Y.; Woortman, A. J. J.; Alberda van Ekensteina, G. O. R.; Loos, K. A biocatalytic
733 approach towards sustainable furanic–aliphatic polyesters. *Polym. Chem.* **2015**, *6*, 5198-5211.
- 734 66. Haernvall, K.; Zitzenbacher, S.; Amer, H.; Zumstein, M. T.; Sander, M.; McNeill, K.;
735 Yamamoto, M.; Schick, M. B.; Ribitsch, D.; Guebitz, G. M. Polyol Structure Influences
736 Enzymatic Hydrolysis of Bio-Based 2,5-Furandicarboxylic Acid (FDCA) Polyesters.
737 *Biotechnol. J.* **2017**, *12*, 1600741.

- 738 67. Papageorgiou, G. Z.; Papageorgiou, D. G.; Terzopoulou, Z.; Bikiaris, D. N. Production of bio-
739 based 2,5-furan dicarboxylate polyesters: Recent progress and critical aspects in their
740 synthesis and thermal properties. *Eur. Polym. J.* **2016**, *83*, 202-229.
- 741 68. Tsanaktis, V.; Terzopoulou, Z.; Nerantzaki, M.; Papageorgiou, G. Z.; Bikiaris, D. N. New
742 poly(pentylene furanoate) and poly(heptylene furanoate) sustainable polyesters from diols
743 with odd methylene groups. *Mater. Lett.* **2016**, *178*, 64-67.
- 744 69. Diao, L.; Su, K.; Li, Z.; Ding, C. Furan-based co-polyesters with enhanced thermal properties:
745 poly(1,4-butylene-co-1,4-cyclohexanedimethylene-2,5-furandicarboxylic acid) [RSC Adv.](#)
746 **2016**, *6*, 27632-27639.
- 747 70. Cottrell, T. L. *The Strengths of Chemical Bonds*, Butterworths, 2nd ed., London, 1958.
- 748 71. Martinez-Tong, D. E.; Soccio, M.; Robles-Hernández, B.; Guidotti, G.; Gazzano, M.; Lotti,
749 N.; Alegria, A. Evidence of Nanostructure Development from the Molecular Dynamics of
750 Poly(pentamethylene 2,5-furanoate). *Macromolecules* **2020**, *53*, 10526-10537.
- 751 72. Araujo, C. F.; Nolasco, M. M.; Ribeiro-Claro, P. J. A.; Rudic, S.; Silvestre, A. J. D.; Vaz, P.
752 D.; Sousa, A. F. Inside PEF: chain conformation and dynamics in crystalline and amorphous
753 domains. *Macromolecules* **2018**, *51*, 3515–3526.
- 754 73. Patkar, M.; Jabarin, S. A. Effect of diethylene glycol (DEG) on the crystallization behavior
755 of poly(ethylene terephthalate) (PET). *J. Appl. Polym. Sci.* **1993**, *47*, 1749-1763.
- 756 74. Soccio, M.; Lotti, N.; Finelli, L.; Gazzano, M.; Munari, A. Aliphatic poly(propylene
757 dicarboxylate)s: Effect of chain length on thermal properties and crystallization kinetics.
758 *Polymer* **2007**, *48*, 3125-3136.
- 759 75. Liang, H.; Hao, Y.; Liu, S.; Zhang, H.; Li, Y.; Dong, L.; Zhang, H. Thermal, rheological, and
760 mechanical properties of polylactide/poly(diethylene glycol adipate). *Polym. Bull.* **2013**, *70*,
761 3487–3500.
- 762 76. Cao, A.; Okamura, T.; Nakayama, K.; Inoue, Y.; Masuda, T. Studies on syntheses and
763 physical properties of biodegradable aliphatic poly(butylene succinate-co-ethylene

- 764 succinate)s and poly(butylene succinate-co-diethylene glycol succinate)s. *Polym. Degrad.*
765 *Stab.* **2002**, *78*, 107-117.
- 766 77. Zeng, J. B.; Huang, C. L.; Jiao, L.; Lu, X.; Wang, Y. Z.; Wang, X. L. Synthesis and Properties
767 of Biodegradable Poly(butylene succinate-co-diethylene glycol succinate) Copolymers. *Ind.*
768 *Eng. Chem. Res.* **2012**, *51*, 12258–12265.
- 769 78. Rudyak, V. Y.; Gavrilov, A. A.; Guseva, D. V.; Tung, S. H.; Komarov, P. V. Accounting for
770 π - π stacking interactions in the mesoscopic models of conjugated polymers. *Mol. Syst. Des.*
771 *Eng.* **2020**, *5*, 1137.
- 772 79. Sago, T.; Itagaki, H.; Asano, T. Onset of Forming Ordering in Uniaxially Stretched
773 Poly(ethylene terephthalate) Films Due to π - π Interaction Clarified by the Fluorescence.
774 *Macromolecules* **2014**, *47*, 217–226.
- 775 80. Shanavas, A.; Sathiyaraj, S.; Chandramohan, A.; Narasimhaswamy, T.; Sultan Nasar, A.
776 Isophthalic acid based mesogenic dimers: Synthesis and structural effects on mesophase
777 properties. *J. Mol. Struct.* **2013**, *1038*, 126-133.
- 778 81. Mahendrasingam, A.; Blundell, D. J.; Martin, C.; Urban, V.; Narayanan, T.; Fuller, W. Time
779 resolved WAXS study of the role of mesophase in oriented crystallisation of poly(ethylene
780 terephthalate-co-isophthalate) copolymers. *Polymer* **2005**, *46*, 6044-6049.
- 781 82. Nolasco, M. M.; Araujo, C. F.; Thiyagarajan, S.; Rudić, S.; Vaz, P. D.; Silvestre, A. J. D.;
782 Ribeiro-Claro, P. J. A.; Sousa, A. F. Asymmetric Monomer, Amorphous Polymer? Structure–
783 Property Relationships in 2,4-FDCA and 2,4-PEF. *Macromolecules* **2020**, *53*, 1380–1387.
- 784 83. (Burgess, S. K.; Leisen J. E.; Kraftschik, B. E.; Mubarak, C. R., Kriegel, R. M.; Koros, W. J.
785 Chain Mobility, Thermal, and Mechanical Properties of Poly(ethylene furanoate) Compared
786 to Poly(ethylene terephthalate). *Macromolecules* **2014**, *47*, 1383–1391.
- 787 84. Bourdet, A.; Esposito, A.; Thiyagarajan, S.; Delbreilh, L.; Affouard, F.; Knoop, R. J. I.;
788 Dargent, E. Molecular Mobility in Amorphous Biobased Poly(ethylene 2,5-

- 789 furandicarboxylate) and Poly(ethylene 2,4-furandicarboxylate). *Macromolecules* **2018**, *51*,
790 1937–1945.
- 791 85. Hedenqvist, M. S. Barrier Packaging Materials, in: Kutz, M. (Ed.), *Handbook of*
792 *Environmental Degradation of Materials*, Elsevier Inc., 2nd ed., **2012**, pp. 833–860.
- 793 86. Burgess, S. K.; Kriegel, R. M.; Koros, W. J. Carbon dioxide sorption and transport in
794 amorphous poly (ethylene furanoate). *Macromolecules* **2015**, *48*, 2184–2193.
- 795 87. Guidotti, G.; Genovese, L.; Soccio, M.; Gigli, M.; Munari, A.; Siracusa, V.; Lotti, N. Block
796 Copolyesters Containing 2,5-Furan and trans-1,4-Cyclohexane Subunits with Outstanding
797 Gas Barrier Properties. *Int. J. Mol. Sci.* **2019**, *20*, 1–15.
- 798 88. Guidotti, G.; Soccio, M.; Lotti, N.; Gazzano, M.; Siracusa, V.; Munari, A. Poly (propylene 2,
799 5-thiophenedicarboxylate) vs. Poly (propylene 2, 5-furandicarboxylate): Two examples of
800 high gas barrier bio-based polyesters. *Polymers* **2018**, *10*, 785.
- 801 89. Guidotti, G.; Gigli, M.; Soccio, M.; Lotti, N.; Gazzano, M.; Siracusa, V.; Munari, A. Ordered
802 structures of poly (butylene 2, 5-thiophenedicarboxylate) and their impact on material
803 functional properties. *Eur. Polym. J.* **2018**, *106*, 284–290.