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Effect of ferulic acid derivative concentration on the release kinetics, antioxidant capacity, and thermal behaviour of different polymeric films

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20 **Abstract**

21 Ferulic acid displays poor thermal resistance during extrusion and compression moulding,
22 slow 2,2-diphenyl-1-picrylhydrazyl (DPPH) reaction kinetics, and undetected release from
23 polylactide (PLA) and polyhydroxyalkanoates (PHA)-based films into polar mediums. Thus,
24 in this study, a ferulic acid derivative Bis-*O*-dihydroferuloyl-1,4-butanediol (BDF) was used
25 as an active additive (up to 40 w%) in PLA, poly(3-hydroxybutyrate) (PHB), and poly(3-
26 hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) matrices to produce blends by extrusion.
27 These blends were then used to prepare films by solvent casting. The BDF displayed good
28 stability with 86-93% retention. The release kinetics in Food Simulant A revealed higher
29 BDF release amounts (1.16-3.2%) for PHA-based films as compared to PLA. The BDF
30 displayed faster DPPH reaction kinetics as compared to ferulic acid. The PHA-based films
31 containing BDF displayed > 80% of DPPH inhibition. The growth of crystals inside polymer
32 matrix had a nucleation effect which reduced the glass transition temperature of the films.

33 **Keywords:** Release kinetics; mathematical modelling; ferulic acid derivative; PHAs and
34 PLA; antioxidant activity; thermal behavior

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42 **1. Introduction**

43 Petroleum-based plastics have surpassed most man-made materials, leading to a global
44 environmental crisis. For example, plastic production accounts for ~40% of the total
45 production of the packaging industry, encouraging the food packaging industry to seek more
46 sustainable materials as alternatives for ensuring food quality and safety (Foschi and Bonoli,
47 2019). Biodegradable bioplastics represent an alternative way to develop sustainable food
48 packaging (Foschi and Bonoli, 2019).

49 Polylactide (PLA) has recently gained tremendous attention in the food packaging industry
50 due to its safety, compostability under controlled conditions, sustainability, and
51 biocompatibility. PLA is a renewable linear thermoplastic polyester that is produced by ring-
52 opening polymerization of lactide at the industrial scale (Rojas et al., 2021). However, low
53 thermal resistance and inherent brittleness restrict its application in food packaging (Ordoñez,
54 Atarés, and Chiralt, 2022a). Other thermoplastic polyesters include polyhydroxyalkanoates
55 (PHAs), such as poly(3-hydroxybutyrate) (PHB) are intracellular energy and carbon storage
56 compounds found in some soil bacteria and possess similar melting temperatures as petro-
57 chemical based plastics i.e., polypropylene (Carboué et al., 2022). However, due to the low
58 glass transition temperature (1-10 °C), the PHB is highly brittle in nature (Fiorese et al.,
59 2009). Nonetheless, the copolymer poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV)
60 can serve as an alternative to PHB because of its higher biocompatibility, lower melting
61 temperature, and comparatively lower crystallinity. However, low thermal stability and
62 difficult processability limit its application in the food industry (Ibrahim, Alsafadi, Alamry,
63 and Husseini, 2021). In this sense, their functional properties can be enhanced by
64 incorporating active compounds as additives into the polymer matrix which not only add
65 value to the material, and increase its competitiveness in the packaging market, but also
66 enhance the ability of the packaging for food preservation.

67 An interesting area in food packaging is the development of active releasing systems. Active
68 releasing packaging is a novel interaction between the packaging and the food product by
69 releasing active compounds from the polymer matrix into the food surface to extend its shelf
70 life (Tawakkal, Cran, Miltz, and Bigger, 2014). One of the biggest challenges in developing
71 an active releasing system is to modulate its ability to release bioactive compounds in an
72 optimum concentration to restrict the nutritional losses owing to oxidation reactions. For
73 instance, ferulic acid is a hydroxycinnamic acid present in plant cell and possess a variety of
74 biological activities i.e., antimicrobial, antioxidant, and anticancer, and is commonly used as
75 an additive for the manufacturing of PLA and PHA-based active releasing films by using
76 extrusion, compression moulding, and melt-blending (Hernández-García, Vargas, and
77 Chiralt, 2022). Several studies have reported improved mechanical, barrier, optical, thermal,
78 and biodegradable properties due to the addition of ferulic acid into PLA and PHA-based
79 systems (Ordoñez et al., 2022a; Ordoñez, Atarés, and Chiralt, 2022b). However, a loss of
80 ~30% of the ferulic acid mass has been reported during the preparation of the active
81 PLA/PHA-based releasing systems due to the presence of one phenolic hydroxyl group
82 (Ordoñez et al., 2022a). Another drawback of incorporating ferulic acid in PLA blends is
83 their non-detectable release into the polar food simulants (i.e., Food Simulant A; which are
84 used to mimic fruits and vegetables) due to the nature, structure, and interactions between the
85 polymer and the bioactive, on the other hand, absence of polymer relaxation could also
86 promote non-detectable ferulic acid release behaviour (Ordoñez et al., 2022a). Furthermore,
87 the slow antioxidant reaction kinetics of ferulic acid due to its monophenolic structure can
88 hinder its application as a package to restrict oxidation kinetics (Goujot, Cuvelier, Soto, and
89 Courtois, 2019).

90 Ferulic acid can be modified to produce ferulic acid derivatives such as Bis-*O*-
91 dihydroferuloyl-1,4-butanediol (BDF) which can have a positive impact on the mechanical,

92 thermal, and biodegradation properties of PHA and PLA-based materials, and maybe on the
93 release kinetics and antioxidant capacity (Carboué et al., 2022; Pion, Reano, Ducrot, and
94 Allais, 2013; Raghuwanshi et al., 2022). For instance, the addition of 40 w% BDF content
95 into PLA and PHA blends improved the elongation at break 82 and 4 times more respectively
96 as compared to the neat samples (Gallos et al., 2021; Longé et al., 2022). Similarly, the
97 addition of BDF (5-40 w%) into PHB blends resulted in faster biodegradation (1.3-3 times)
98 of the PHB/BDF blends by *Actinomucor elegans* in the soil as compared to neat PHB
99 samples; since fungi can degrade and metabolize hydroxycinnamic acids i.e., ferulic acids
100 which are a structural compound in the lignocellulosic matrix (Carboué et al., 2022). The
101 BDF molecule can provide detectable release from PLA/PHA matrices into polar mediums
102 by causing polymer relaxation due to its plasticizing properties or by affecting the polymer's
103 glass transition temperature. On the other hand, the presence of bi-phenolic OH-groups in the
104 BDF additive can improve the thermal resistance and antioxidant capacity of both additive
105 and the polymeric system (Longé et al., 2022). For instance, BDF displayed higher thermal
106 resistance with a mass loss of 10% at 285-298°C as opposed to 205-210°C of ferulic acid.
107 Ferulic acid derivatives i.e., BDF are also thermally stable during extrusion and injection
108 processes (175-185°C) (Kasmi, Gallos, Beaugrand, Paës, and Allais, 2019). Similarly, the
109 antioxidant reaction kinetics of BDF can be much faster than ferulic acid due to its modified
110 structure since ferulic acid requires the formation of biferulic acid before reducing 2,2-
111 diphenyl-1-picrylhydrazyl (DPPH·) radical (Aragón-Gutiérrez et al., 2020; Goujot et al.,
112 2020).

113 The release kinetics and the partition coefficient of the active compound from the polymer
114 matrix into the complex food systems are greatly influenced by the additive-polymer
115 interactions, potential relaxation of the polymer upon contact with the food simulant, and the
116 chemical affinity of the compounds toward polymer/food simulant. These factors define the

117 concentration of the bioactive in the simulant as a function of time. Contrarily, the release of
118 the active compound is influenced by the polymer nature, the environmental conditions, and
119 the molecular characteristics of the additive; for instance, the release rate is faster when
120 governed by swelling and slower when governed by diffusion in the polymer matrix
121 (Ordoñez et al., 2022a; Requena, Vargas, and Chiralt, 2017). Therefore, the development of
122 active PLA, PHB, and PHBV films containing BDF requires the verification of the influence
123 of bioactive on the functional attributes of the polymer as well as on the efficient release to
124 exert the antioxidant effect on a particular system. Since there was no study on the influence
125 of BDF concentration on different polymeric films, the objective of this study was to develop
126 PLA, PHB, and PHBV films with BDF at different concentrations (0, 10, 20, and 40 w%) for
127 packaging applications. The influence of BDF incorporation on the release kinetics was
128 investigated in the polar medium. Furthermore, the chemical structure was evaluated to
129 understand the dynamics of chemical fingerprinting before and after release kinetics.
130 Antioxidant capacity was analysed by using DPPH reaction kinetics as a benchmark. Finally,
131 thermal properties were also investigated.

132 **2. Materials and methods**

133 **2.1. Materials**

134 PHB and PHBV powder were acquired from BIOMER (Schwalbach am Taunus, Germany).
135 The PLA was purchased from NatureWorks (IngeoTM 4043D, Minnesota, USA). The BDF
136 was synthesised from ferulic acid with a protocol described elsewhere (Pion et al., 2013). 2,2-
137 diphenyl-1-picrylhydrazyl (DPPH) was acquired from Fischer Scientific (Illkirch, France).
138 Ethanol and chloroform were purchased from VWR Chemicals BDH (Radnor, PA, USA). All
139 other reagents used were of analytical grade.

140 **2.2. Methods**

141 **2.2.1. Preparation of polymer/BDF specimens by extrusion**

142 Extrusion of the polymer/BDF blends was performed by the method given by Longé et al.
143 (2022) by using a compounding twin screw extruder HAAKE MiniLab II (Thermo Fischer
144 Scientific, Waltham, MA, USA). Briefly, blends with polymers (PHB or PHBV) and BDF
145 weight ratios (100:0, 90:10, 80:20, and 60:40) were extruded at 170°C at 60 rpm by setting
146 the screws in co-rotation. While for PLA samples 180°C at 50 rpm was used (Gallos et al.,
147 2021). The moulding of the samples was carried out by the HAAKE MiniLab Pro Piston
148 Injection Moulding System. A DMA test bar mould was used with dimensions of 60 mm ×
149 10 mm × 1 mm. During the injection, 45 °C temperature was used to maintain the mould.

150 **2.2.2. Film preparation**

151 The solvent casting method given by Carboué et al. (2022) was used with slight
152 modifications to prepare the different film samples (PHBV.BDF, PHB.BDF, and PLA.BDF).
153 Briefly, the polymer/BDF blends (533 mg) obtained previously were dissolved in chloroform
154 (26.6 mL) and the solution was then poured into stainless steel rectangular moulds
155 (Dimensions: 7.5 cm × 2.5 cm). To obtain uniform film samples, the solvent was evaporated
156 at room temperature under a fume hood. The steel moulds were covered with cardboard to
157 prevent the effect of the hood from destabilizing the films.

158 **2.2.3. Retention of bioactive in the films after processing**

159 The remaining content of BDF in the films was determined by a method given by Woranuch,
160 Yaksan, and Akashi (2015) with modifications. In brief, BDF in each film sample (1 cm²)
161 was extracted with 10 mL of chloroform at 40 °C for 48 h. The extracted solution was then
162 analysed by using a UV-VIS spectrophotometer (Cary 60, Agilent Technologies, CA, USA)
163 at a wavelength of 280 nm. The remaining content was calculated by using a standard
164 calibration curve ($y = 0.0013x$, $R^2 = 0.9904$).

165 **2.2.4. Release kinetics of BDF**

166 The specific migration of BDF from different polymeric films was evaluated by using Food
167 Simulant A (10% ethanol) according to European Commission (EC) regulation 10/2011
168 (since Food Simulant A can be used to mimic fruits and vegetables) by following the protocol
169 previously established by Khan, Volpe, Salucci, Sadiq, and Torrieri (2022) with slight
170 modifications. The film samples (4 cm²) were completely immersed (double-sided) into the
171 food simulant at room temperature. The UV-VIS Spectrophotometer (Cary 60, Agilent
172 Technologies, CA, USA) was used to determine the concentration of BDF released from the
173 films into the simulant at 280 nm. The samples were taken out at regular intervals of time (0,
174 24, 48, 144, 216, and 240 h) to quantify the concentration of the bioactive by using a standard
175 calibration curve for BDF (150-600 µg/mL). The results were expressed as µg/mL of the
176 simulant.

177 **2.2.5. Mathematical modelling**

178 The mathematical models are useful in describing the release behaviour of a bioactive from
179 the polymeric chains of a film into the food simulant by using Fick's Second Law. The
180 migration process was elucidated by the diffusion coefficient (D) and partition coefficient (K)
181 of the migrant molecules. The following assumptions were considered by using a relationship
182 derived from Fick's Second Law for a plane sheet to determine the diffusion coefficient of
183 BDF from the experimental data (Niaz and Imran, 2021): a) initial concentration of BDF was
184 homogenous throughout the film, b) the material was homogenous and isotropic, c) initial
185 concentration of the BDF was zero in the food simulant solution, d) influence of swelling
186 upon the kinetics of mass transfer was supposed negligible, e) the amount of BDF diffused
187 from the film into simulant was increased in the concentration of the migrant from zero ($C_{f,0}$)
188 to equilibrium ($C_{f,\infty}$), and f) the effective diffusivity should be considered constant. This

189 model considered a limited volume of a plane sheet (film) in a limited volume of solution
 190 (food simulant), and if we consider that diffusion occurred from both sides of the film; Fick's
 191 Law can be solved numerically rather than analytically by using finite differences
 192 methodology (in which we solve the non-linear terms of the partial differential equation
 193 (PDE), where the unknown variable is the migrant concentration at each nodal point of the
 194 system). The Fick's Model, boundary conditions, and differential equations are as follows:

$$195 \quad \frac{\partial C(x,t)}{\partial t} = D \left[\frac{\partial^2 C(x,t)}{\partial x^2} \right] \quad (1)$$

$$196 \quad \left\{ \begin{array}{l} \left. \frac{dc_i(t)}{dt} \right|_{i=0} = 0 \\ \left. \frac{dc_i(t)}{dt} \right|_{i=n} = 0 \end{array} \right. \quad (2)$$

197 Whereas C is the ratio of the concentration of BDF at time t and its concentration after
 198 infinity. Furthermore, to simplify the solution of PDE of the Fick's Law, the method of lines
 199 was used with respect to the spatial variable on the second derivative. This approximation
 200 transforms the PDE into an ordinary differential equation (ODE):

$$201 \quad \frac{dc_i t}{dt} = D \frac{(c_{i-1}(t) - 2c_i(t) + c_{i+1}(t))}{x^2} \quad (3)$$

202 x is the distance from the interface obtained by dividing the thickness of the film (e) to the
 203 total number of layers (η).

$$204 \quad C = \frac{M_{f,t}}{M_{f,\infty}} \quad (4)$$

$$205 \quad x = \frac{e}{\eta} \quad (5)$$

206 For ensuring the validation of mathematical models and to ensure the goodness of fit of the
 207 predicted data with experimental by minimizing the sum of square of the differences between

208 measured and predicted values, root mean square error (RMSE) was calculated by using
209 MATLAB (version R2022a, MathWorks, USA).

$$210 \quad RMSE = \sqrt{\frac{\sum_{i=1}^N (\hat{y}_i - y_i)^2}{N}} \quad (6)$$

211 Where \hat{y}_i and y_i are the residual values of observed and predicted values respectively while
212 N is the number of the experimental point (Khan et al., 2022).

213 Partition coefficient can be described as the ratio of the BDF in the food simulant ($C_{s,\infty}$) to the
214 BDF in the polymer matrix ($C_{f,\infty}$) once plateau is reached:

$$215 \quad K = \frac{C_{s,\infty}}{C_{f,\infty}} \quad (7)$$

216 **2.2.6. Fourier-transform infrared (FT-IR) spectroscopy**

217 The chemical fingerprinting of all the film samples before and after release kinetics was
218 evaluated through Fourier-transform infrared (FT-IR) spectroscopy by using FT-IR
219 Spectrometer (Cary 630, Agilent Technologies, CA, USA). The spectra were recorded in the
220 middle infrared ($4000-650 \text{ cm}^{-1}$) range using absorbance mode with a resolution of 4 cm^{-1} .
221 For each spectrum, 8 scans were co-added.

222 **2.2.7. Antioxidant activity**

223 The DPPH radical scavenging method is a globally followed and accepted method for
224 measuring the antioxidant capacity of the polymeric materials. The methodology is based on
225 the reduction of a stable DPPH radical by means of an antiradical compound as a function of
226 time (Khan, Di Giuseppe, Torrieri, and Sadiq, 2021). However, there are certain assumptions
227 that should be kept in mind while measuring the antioxidant capacity of a compound: a) the
228 antioxidant capacity of an antioxidant depends upon its chemical structure, b) the reaction can
229 be fast ($< 30 \text{ min}$), slow ($> 60 \text{ min}$), or moderate ($30-60 \text{ min}$) depending upon the ability of

230 antioxidant to reduce the DPPH[•] radical, c) contact time of the antioxidant with DPPH radical
231 should be respected as the antioxidant molecules will not be able to express all the
232 antioxidant activity and will remain unused, thus we will have incorrect antioxidant capacity,
233 d) choice of solvent affect the kinetics parameters i.e., the balance between HAT and SET
234 mechanism, and e) ferulic acid is a slow antioxidant due to its monophenolic structure, while
235 BDF a derivative of ferulic acid can display better reaction rate due to diphenolic structure
236 (Goujot et al., 2019).

237 Considering the above facts, the antioxidant activity of the film samples was measured by
238 method given Priyadarshi, Kim, and Rhim (2021) with modifications. Briefly, an ethanolic
239 solution of DPPH was prepared by dissolving 2.5 mg of DPPH in 100 ml of ethanol. 1 cm² of
240 each film sample was added into 10 ml of ethanol, incubated for two different contact times
241 (30 min and 90 min) in the dark at room temperature and the absorbance was measured at
242 517 nm. The same test without a film sample was used as a control. The antioxidant capacity
243 of the film samples was calculated as percentage DPPH inhibition and was as follows:

$$244 \text{ Antioxidant activity (\%)} = \frac{AC-AS}{AC} \times 100 \quad (8)$$

245 Where AC (0.6551) is the absorbance of the control and AS is the absorbance of the sample.

246 **2.2.8. Thermal analysis**

247 *Thermogravimetric analysis (TGA)*

248 TGA was performed by using TGA Q500 (TA Instruments, NC, USA) under nitrogen flow.
249 Approximately, 3-7 mg of the film samples were equilibrated at 50 °C for 30 min. Then the
250 samples were heated from 50 °C to 500 °C at 10 °C/min. The results were presented as
251 graphs representing weight loss of the film samples as opposed to temperature.

252 *Differential scanning calorimetry (DSC)*

253 DSC was performed by using a DSC Q20 (TA Instruments, NC, USA). ~4-10 mg film
254 samples were placed in a sealed pan flushed with pure nitrogen gas. The first heating scan
255 was performed from -80 °C to 200 °C at a heating rate of 10°C/min and was used to
256 determine the melting temperature (T_m). This was followed by a cooling run to -80°C with a
257 cooling ramp of 200°C/min. The glass transition temperature (T_g) was obtained during the
258 second heating scan from -80 °C to 200 °C at 10 °C/min rate (Carboué et al., 2022).

259 **2.2.9. Statistical analysis**

260 One-way analysis of variance (ANOVA) and independent t-test were performed to estimate
261 the significant difference ($p < 0.05$) among mean observations (SPSS, version 27.0, Chicago,
262 IL, USA). All the experiments were performed in triplicates.

263 **3. Results and discussion**

264 **3.1. Quantification of BDF in the films**

265 The quantification of the final amount of BDF remaining in the active films is important
266 since at high temperatures during extrusion process significant losses of bioactive compounds
267 can occur due to thermal degradation or chemical reaction i.e., cross-linking or
268 transesterification. It was observed that similar amount of BDF was recovered from each film
269 sample (PHB and PHBV) indicating good homogeneity of BDF at macromolecular level.
270 However, the total amount of BDF recovered from films with 10 w%, 20 w% and 40 w%
271 BDF content was only $89.85 \pm 1.61\%$, $91.40 \pm 0.32\%$, and $93.42 \pm 2.11\%$, respectively of the
272 initial amount introduced during the extrusion process, and irrespective of the polymeric
273 material used (PHB and PHBV). However, for PLA the total amount of BDF recovered was
274 $86.50 \pm 3.13\%$, $89.96 \pm 0.75\%$, and $91.70 \pm 0.38\%$. Thus, the thermal process induced ~6.5-
275 13.5% of BDF mass loss, that could be attributed to both thermal degradation, chemical
276 interactions, and oxidation reactions since no volatile compounds are generated at such high

277 temperatures (i.e., 170-180 °C). It can be observed that the amount of remaining BDF
278 increased with increasing concentration of BDF in the films, this phenomenon has already
279 been reported for ferulic acid-based EVOH (ethylene vinyl alcohol) films which underwent
280 melt extrusion at 180 °C (Aragón-Gutiérrez et al., 2020). According to Ramos, Jiménez,
281 Peltzer and Garrigós (2014) residence time of mixture in the extruder, additive concentration,
282 degree of volatility of the additive, and extrusion temperature are the main factors affecting
283 the final concentration of the additive in the blend. A loss of 30-40% have been reported for
284 the polymeric materials containing ferulic acid in literature after melt/blown extrusion,
285 however we only observed ~13.5% BDF loss because BDF contains two phenolic hydroxyl
286 groups as opposed to ferulic acid which contains only one, thus show more thermal stability
287 than ferulic acid. The TGA results also validated this fact since ferulic acid displayed a mass
288 loss of 10% at ~210 °C as opposed to BDF which displayed similar mass loss at ~290°C
289 (Aragón-Gutiérrez et al., 2020; Santos et al., 2012). These results were in accordance with
290 results observed for thermo-processed PLA films containing ferulic acid (Ordoñez et al.,
291 2022a).

292 **3.2. Release kinetics of BDF**

293 Release kinetics of a bioactive compound is important to study since not only it has a role in
294 controlling the quality of the food product but also in meeting the migration limits set by
295 regulatory authorities. To mimic the fruits and vegetables, 10% ethanol was selected as a
296 Food simulant (Food simulant A) to elucidate the release of BDF from the film into the
297 simulant. Fig 1. displays the release of different BDF concentrations from different polymeric
298 materials (i.e., PHBV, PHB, and PLA). There was a significant difference ($p < 0.05$) in the
299 amount of BDF released with increasing concentration of BDF in the matrix. A significant
300 increase in the release of BDF was observed from all the film samples in the initial 48 h,
301 followed by equilibrium. The highest concentration of BDF released was (465 µg/mL, 759

302 $\mu\text{g/mL}$, and 101 $\mu\text{g/mL}$) observed for film samples containing 20 w% BDF (PHBV, PHB,
303 and PLA respectively) irrespective of the polymer type used. The polymer and bioactive
304 nature, structure, and affinity toward food simulant are some of the parameters that influence
305 the release of bioactive from the film into the simulant (Khan et al., 2022). In accordance
306 with the above fact, the films with low BDF concentration (i.e., 10-20 w%) displayed a better
307 release percentage ($p < 0.05$) as compared to films with the highest BDF content (40 w%),
308 because BDF is hydrophobic in nature thus a lower amount means it has more affinity for
309 hydrophilic food simulant (i.e., 10% ethanol) thus more release can be expected.
310 Furthermore, a higher percentage of BDF (40%) favoured the BDF-BDF interaction rather
311 than the BDF-PHA interaction along with the formation of a crosslinking cluster of PHA-
312 BDF-BDF-PHA structure that leaves the BDF trapped and then delays its release. The films
313 with more BDF content are more elastomeric than the ones with a smaller amount which
314 could be due to the π - π stacking between the aromatic rings of the BDF molecules. Still, the
315 released amounts were extremely low because of the nature of the simulant used.

316 In the case of PLA based systems, a release of < 0.5 w% of BDF could be due to several
317 reasons a) polarity of the polymer/additive/simulant, b) PLA has better affinity for aromatic
318 compounds as compared to PHAs due to its structure, c) as reported by Ordoñez et al.
319 (2022a) during thermal processing partial esterification of -OH end chain of PLA with ferulic
320 acid could occur which can limit the compound release into the simulant, however this was
321 not the case in our study, since no transesterification occurred as confirmed by NMR (Gallos
322 et al., 2021), d) only $\geq 50\%$ ethanol can cause relaxation of PLA matrix by penetrating
323 polymer matrix and favouring the release of the bioactive, and e) molecular mobility and
324 diffusion-controlled mass transfer could be limited due to glassy-state of the polymer in the
325 absence of polymer relaxation at the release temperature, however at 40% w BDF content
326 π - π stacking between the aromatic rings of the BDF molecules was promoted which could

327 restrict the release of BDF from the PLA films in amorphous phase (Ducruet, Domenek,
328 Colomines, and Guinault, 2009; Ordoñez et al., 2022a).

329 On the other hand, PHB and PHBV displayed better release amounts (0.59-3.2%) because: a)
330 they are not in their glassy state and polymer relaxation up to some extent can be expected, b)
331 both polymers and additives are hydrophobic in nature, and c) PHB showed a better release
332 percentage than PHBV because PHB is more crystalline and brittle whereas PHBV contain
333 more hydroxyvalerate monomers (Aramvash et al., 2016). Furthermore, the BDF started to
334 hinder PHB crystallization at ≥ 20 w% content which could be correlated with better release
335 of PHB as compared to PHBV (Longé et al., 2022).

336 On the other hand, no polymer swelling, relaxation, and degradation were observed for PLA-
337 based films as opposed to what was reported in the literature due to the influence of ethanol-
338 rich solutions on the polymer matrix, thus it is safe to say that swelling-controlled model is
339 not applicable in our scenario (Ordoñez et al., 2022b). Ordoñez et al. (2022a) similarly,
340 reported $< 15\%$ release of ferulic acid but in D1 food simulant since the phenolic OH-group
341 in ferulic acid could form hydrogen bond through oxygen of ester group of the polymer, thus
342 limiting the diffusion even in hydrophobic mediums.

343 **3.3. Mathematical modelling**

344 As mathematical models are useful in describing the release phenomena, they can be used to
345 estimate the ability of an active package to restrict the oxidation kinetics. In this study, Fick's
346 Second Law was solved numerically by using finite differences methodology for fitting of the
347 experimental data and to describe the release of BDF from the film into the simulant. The
348 experimental values of M_t/M_∞ as well as the fitted Fick's Model are shown in Fig 1. The
349 effective diffusivity for PHBV samples decreased linearly ($p < 0.05$) with increasing
350 concentration of BDF in the polymer matrix because of increasing hydrophobicity and lower

351 affinity for 10% ethanol which is relatively hydrophilic in nature. The D value is related to
352 molecular mobility of the additive within polymer matrix and is influenced by several factors
353 i.e., structural characteristics of the matrix, molecular weight of the additive, and solubility of
354 the antioxidant compound (Benbettaïab, Assifaoui, Karbowiak, Debeaufort, and Chambin,
355 2016). Similarly, PHB samples with low BDF content (10-20 w%) displayed higher (2.2-2.5
356 times) D values as compared to the ones with highest BDF concentration. Similar trend was
357 also observed for PLA films (Table 1). The higher retention can be correlated with the ability
358 of BDF to establish charge-charge interactions with the polymer (Benbettaïab, Tanner, Cayot,
359 Karbowiak, and Debeaufort, 2018). The PHB, PLA, and PHBV might interact with BDF
360 through hydrogen bonding, dipole-dipole and dipole-charge. The mathematical models
361 adequately described the release mechanism of BDF from different polymer systems
362 indicating good linearity and fitting of experimental data with the model data with RMSE <
363 0.1 and $R^2 > 0.85$ (Khan et al., 2022). Our results are in accordance with the literature in
364 which authors observed a fluctuating diffusion coefficient which was dependent on the
365 polarity and concentration of the bioactive (Marvdashti, Yavarmanesh, and Koocheki, 2019;
366 Ordoñez et al., 2022a). A very low partition coefficient (K) values were observed in our study
367 for all the film samples (< 0.03) which indicates that BDF has more affinity for the film
368 samples as compared to the food simulant since BDF has two phenolic OH groups which can
369 allow it to interact perfectly with hydrophobic polymer matrix i.e., PLA and PHAs. We
370 observed a limited release (< 3.5% of the content present in the film) of BDF from all
371 packaging materials, in contrast to release of ferulic acid (for which ~8-15% have been
372 reported) from PLA and PHBV systems due to differences in their structure, polarity of the
373 simulant, and the temperature of release kinetics experiment (Hernández-García et al., 2022).
374 A slow and limited release of the bioactive can restrict the active role of the additive in
375 different food systems with high polarities. In our scenario, since no conventional plasticizer

376 was added to the system apart from gaining advantage of the plasticizing properties of BDF
377 (which don't seem enough to promote release), a conventional plasticizer i.e.,
378 glycerol/sorbitol can provoke the structural relaxation of polymer matrix and improve
379 molecular mobility to promote diffusion (Longé et al., 2022; Ordoñez et al., 2022a).

380 **3.4. FT-IR**

381 The chemical finger printing of all the film samples to identify functional groups of interest
382 and their interaction before and after release is presented in Fig 2, 3 and 4. For PHBV
383 samples, the main characteristic C-H stretching bands were observed around 1274 and 2974
384 cm^{-1} (Unalan, Colpankan, Albayrak, Gorgun, and Urkmez, 2016). The absorption band at
385 1274 cm^{-1} can also be assigned to C-O stretch (alkyl aryl ether group). C-H bending
386 vibrations were observed at 1379 cm^{-1} (Unalan et al., 2016). CO and C-CH₃ stretching bands
387 were detected around 1054 and 1044 cm^{-1} , respectively. The most intense PHBV absorption
388 peak at ~1720 cm^{-1} can be associated with C=O stretching vibrations due to crystalline nature
389 of the carbonyl group of PHBV. The presence of CH₂ groups can be validated by the peak
390 around 2932 cm^{-1} . A broad peak between 3440-3450 cm^{-1} can be attributed to O-H stretching
391 vibrations. Similar absorption spectra were observed for PHB films, for instance, C-O
392 stretching at 1053 cm^{-1} , C-H bending at 1378 cm^{-1} , and C=O stretching at 1720 cm^{-1} . On the
393 other hand, for PLA films, two characteristic peaks at 752 and 868 cm^{-1} were observed for
394 crystalline and amorphous phases, respectively. The C=O stretching was observed as a large
395 band at 1748 cm^{-1} . The most prominent peak (1080 cm^{-1}) was the rocking vibration of the
396 helical backbone of CH₂ group. Other absorption peaks noticed were C-O stretching modes
397 (~1180 cm^{-1}), CH₃ bending vibration (~1451 cm^{-1}), CH asymmetric deformation (1358 cm^{-1}),
398 and CH stretching vibration (2995 cm^{-1}) (Siriprom, Sangwanate, Chantarasunthon,
399 Teanchi, and Chamchoi, 2018). After incorporation of BDF into the blend, the C-O, O-H, and
400 C-H stretching vibrations in PHBV and PHB films shifted to a lower wavenumber with

401 reduced intensity with increasing concentration of BDF from 0 to 40 w% (from 1278 to 1228,
402 ~ 3449 to ~ 3336 cm^{-1} , and ~ 2974 to ~ 2932 cm^{-1} respectively), which could be due to weak
403 interactions (dipole-dipole or hydrogen bonding) formed between polymer matrix and BDF.
404 However, after the release kinetics, the aforementioned peaks shifted back again to their
405 original wavenumber possibly due to the release of BDF from the polymeric matrix causing
406 the stretching of O-H and C-H groups upon cleavage by the food simulant. It was reported
407 that stretching of C-H group could also be an indication of hydrogen bond formation between
408 solvent molecules and polymer which can shift the frequency to higher wavenumbers (Kondo
409 and Sawatari, 1996). The O-H stretching can also be an indication of intermolecular
410 hydrogen bonding between OH group of the PHB/PHBV and carboxylic group of the BDF.
411 Similarly, C-H stretch (2930-2980) and O-H bend were also reported be characteristic peaks
412 for ferulic acid (Yerramathi et al., 2021). Disappearance of CH_3 asymmetric deformation
413 after the addition of BDF in both PHB and PHBV films were observed, however, the peaks
414 re-appeared after the release of BDF from the films, which indicates that BDF formed
415 hydrogen bond with methoxy group of PHAs, however, these were easily cleaved by 10%
416 ethanol leading to re-appearance of the peak (Kluth, Sung, and Maboudian, 1997). Contrarily,
417 the spectra in the C-H stretching vibration shifted to lower wavenumber with increasing BDF
418 content from 10-40% (from 2995 to 2943 cm^{-1}) only after its release from PLA films which is
419 an indication of stronger interaction between PLA and BDF which led to significantly lower
420 release than PHAs.

421 **3.5. Antioxidant capacity**

422 The antioxidant capacity of the active films containing BDF was assessed by using the
423 method based on the scavenging of the DPPH \cdot radical molecule. The DPPH-BDF reaction
424 kinetics scheme is presented in the Fig S1 as opposed to the reaction kinetics of ferulic acid

425 with the DPPH (Goujot et al., 2019). It has been already established that ferulic acid is a slow
426 antioxidant and require > 60 min of incubation with the DPPH· radical to finally reach
427 plateau (Benbettaïeb et al., 2018; Goujot et al., 2019), since ferulic acid contains only one
428 aromatic hydroxyl group (AHOH in reaction 1) and can interact with DPPH· radical to form
429 phenoxy radical which in-turn can interact with another DPPH· radical to form diferulic acids
430 (reaction 4) having two hydroxyl groups (Goujot et al., 2019). However, these reactions are
431 not required for the DPPH-BDF interaction since BDF has two phenolic hydroxyl groups and
432 can display faster reaction rate, thus reaction scheme can be modified and presented as in Fig
433 S1. Furthermore, oxidated BDF can be dismutated to regenerate a phenolic group, thus
434 enhancing its antiradical property (Reano et al., 2015). The DPPH· interacted with BDF
435 mainly by SET (single electron transfer) mechanism during which the antioxidant produces
436 phenoxide anion which finally causes the reduction of the DPPH· radical. It has been reported
437 that polar solvents (i.e., ethanol and methanol) can strongly bind with hydrogen atoms and
438 reduce HAT (hydrogen atom transfer) mechanism and promote SET mechanism (Xie and
439 Schaich, 2014). The antioxidant capacity results for control and active films are displayed in
440 Fig 5. The above assumptions were validated by the results shown as there was no significant
441 differences ($p > 0.05$) in the radical scavenging activity of BDF for both contact times since
442 equilibrium reached only after 30 min of incubation. The DPPH radical scavenging activity
443 increased linearly with increasing concentration of the BDF in all the film samples. The
444 PHBV and PHB samples containing 20-40 w% BDF displayed > 80% of DPPH inhibition.
445 However, for PLA film samples containing 20-40 w% BDF it was significantly lower (<
446 75%) which could be due to stronger interaction of PLA with BDF due to its affinity for
447 phenolic compounds. The residual purple colour only appeared in PLA samples with 10%
448 w/w BDF content at the end of both analysis time (30 and 90 min), however, for all other

449 samples a change in colour of the solution from purple to yellow was observed. Since, at low
450 BDF concentrations there were no BDF-BDF interaction which could lead to a higher
451 average percentage inhibition (but still non-significant) for 90 min contact time. However,
452 this was not the case for higher concentrations (≥ 20 w%) (where BDF-BDF interactions or
453 cross-linking cluster Polymer-BDF-BDF-Polymer) can hinder its full potential. The lower
454 film antioxidant activity can be explained by interactions between the film matrix and active
455 molecules in the film, limiting their release. PLA has stronger interactions with bioactives
456 than PHAs so it can also affect the release kinetics and antioxidant properties even in highly
457 hydrophobic mediums. All the control samples displayed extremely low antioxidant capacity
458 ($< 5\%$) which is to be expected from PLA and PHAs since they don't have free residual
459 amino groups, unlike protein/polysaccharide-based macromolecules which can convert free
460 amino groups to ammonium groups by accepting hydrogen ions from DPPH solution. Thus,
461 the BDF molecule has the potential to act as an antioxidant faster than ferulic acid in complex
462 food systems and to inhibit or restrict the nutritional losses caused by oxidation reactions.

463 **3.6. Thermal properties**

464 The TGA curves (%) for control and active films performed under a nitrogen atmosphere are
465 shown in Fig S2. The thermal stability of the polymer is commonly attributed to different
466 parameters i.e., $T_{50\%}$ (temperature at 50% weight loss) and $T_{95\%}$ (temperature at 95% weight
467 loss) (Table S2). The neat PHBV films displayed one-step thermal degradation between 245-
468 280 °C. This thermal degradation was reported to proceed via development of an
469 intermediate (six membered ring ester) having an alkenyl end and a carboxyl end group
470 (Bakare, Bhan, and Raghavan, 2014). However, after incorporation of BDF into the PHBV
471 films the degradation proceeded in two steps, which indicates the formation of linkages
472 between carboxyl group of the intermediate formed and hydroxyl group of the BDF. The
473 highest weight loss (~45%) for PHBV films was observed between 266-277 °C, however,

474 thermal stability significantly improved ($p < 0.05$) after incorporation of BDF into the blend,
475 for example, similar weight loss for PHBV films containing 40% BDF was observed between
476 277-319 °C. The increased thermal stability of the films containing BDF could be due to
477 presence of phenolic OH groups. A similar single-stage decomposition was observed for neat
478 PHB samples between ~250-280 °C due to β -elimination in ester moieties causing breakage
479 of C-O and C=O bonds, which leads to the production of oligomeric acid which in-turn gets
480 converted into crotonic acid and cause reduction in molecular weight (Etxabide et al., 2022).
481 The maximum weight loss for PHB films (45%) was observed between (269-279 °C).
482 However, the degradation occurred in two steps after the addition of BDF in the samples after
483 the mass loss (between 50-95%) occurred at ~1.1-1.15 times higher temperatures as
484 compared to control. However, for the degradation of PLA films occurred in two steps.
485 During the first stage, all film samples were thermally stable till ~80 °C. The weight loss
486 between (80-175 °C) can be attributed to bound moisture on the film surface. The second
487 thermal degradation stage (280-385 °C) can be attributed to polymer back bone breakage due
488 to thermal degradation and displayed maximum weight loss (Sucinda et al., 2021). The
489 weight loss at the end of this stage decreased (from 98.07%, 95.29%, 93.32%, and 92.26%)
490 with increase in the concentration of the BDF from 0, 10, 20, and 40 w% respectively, which
491 indicates strong linkage between BDF and PLA backbone which delayed thermal scission.

492 The DSC analysis was carried out to evaluate the thermal transitions of the films developed.
493 The glass transition and melting temperatures (T_g and T_m) are shown in Table 1. The
494 incorporation of BDF in the film samples brought changes in the thermal properties of the
495 films. A significant decrease ($p < 0.05$) in melting and glass transition temperatures was
496 observed for PHB samples after the incorporation of BDF into the blend which could be due
497 to increased flexibility of the polymeric matrix (Carboué et al., 2022). The presence of BDF
498 probably exerts two contrasting mechanisms to decrease T_g of the films, a) inducing the

499 growth of large number of crystals which could have a nucleation effect on the polymer and
500 b) a decrease in crystal size because of imperfections (López-de-Dicastillo, Gómez-Estaca,
501 Catalá, Gavara, and Hernández-Muñoz, 2012). Similarly, a decrease in T_m and T_g of the PLA
502 samples (from 148.3 to 132.5 °C and 56.2 to 12.2 °C, respectively) was observed with
503 increasing concentration of BDF from 0 to 40 w%. A semi-crystalline behaviour of PLA
504 films was observed with a single T_g , which is an indication of full miscibility of both
505 components in the amorphous phase. While a BDF of more than 20 w% inside polymer
506 matrix led to crystallization due to a lack of interaction with PLA (Gallos et al., 2021). A
507 reduction in T_m could be due to hydrogen interactions between phenolic hydroxyls and
508 polyester carbonyls which can reduce crystal size and melting temperature (Hernández-
509 García et al., 2022). Contrarily, incorporation of coumaric acid and protocatechuic acid (due
510 to their structure) improved the T_g of the PLA and PHBV films due to improved interchain
511 interactions (cross-linking) as compared to ferulic acid which can cause reduction of
512 molecular mobility thus, inhibiting crystallization (Hernández-García et al., 2022). The T_g of
513 the neat PHBV samples was extremely low (-1.66 °C) as expected. A significant decrease in
514 T_g of the PHBV films was observed after the incorporation of BDF up to 20 w%, however,
515 beyond that limit BDF promoted supercooling of the polymer without total crystallization in
516 the film i.e., which is evident with a higher T_g (-8.3 °C) for PHBV films with 40 w% BDF
517 than films with 20 w% BDF (-12.05 °C).

518 **4. Conclusion**

519 The total recovery of the active additive (BDF) in the casted films obtained from extruded
520 blends was relatively high (86-93%) which indicates that these compounds can be
521 incorporated during the usual thermoplastic process in the packaging industry. Although no
522 quantitative release of ferulic acid was detected in the Food Simulant A for the PLA-based
523 films, we quantified the release of BDF from PLA matrix even though it was significantly

524 lower (< 0.5%) as compared to PHB and PHBV due to better affinity of PLA for phenolic
525 acids. The slowest D values were observed for film samples containing 40 w% BDF content
526 which could be correlated with their more hydrophobic nature as compared to lower
527 concentrations. The addition of BDF into the polymeric structure and its release also brought
528 changes in the FT-IR spectra. We observed a comparatively faster DPPH reaction kinetics of
529 the BDF molecule as compared to ferulic acid due to the presence of biphenolic structure.
530 The PHBV and PHB samples containing 20-40 w% BDF displayed > 80% of DPPH
531 inhibition. However, for PLA film samples containing 20-40 w% BDF it was significantly
532 lower (< 75%). The weight loss (between T_{50-95%}) for neat PHBV films containing 40% BDF
533 (277-319 °C) was significantly higher than control (266-277°C) due to formation of linkages
534 between carboxyl group of the intermediate formed during thermal scission of PHBV and
535 hydroxyl group of the BDF. Even though, the slowest release was observed for PLA films,
536 they can have great potential for packaging purposes, however, further release and
537 antioxidant studies into food matrices are required to test the ability of these films in real
538 systems from where polymer relaxation could facilitate compound migration to effectively
539 restrict oxidation kinetics to preserve nutritional quality of food products.

540 **Conflicts of interest statement**

541 The authors declare no conflict of interest.

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Table 1. Melting and glass transition temperatures obtained from DSC curves for different polymeric films

Samples	T_m (°C)	T_g (°C)
PHBV	155.5 (1.3) ^b	-1.66 (0.04) ^c
PHBV.BDF 10%	152.3 (0.8) ^b	-11 (0.90) ^a
PHBV.BDF 20%	147.6 (1.8) ^a	-12.05 (0.42) ^a
PHBV.BDF 40%	152.6 (1.5) ^b	-8.29 (0.25) ^b
PHB	165.2 (1.8) ^{bc}	0.44 (0.08) ^c
PHB.BDF 10%	168.3 (1.5) ^c	1.16 (0.09) ^c
PHB.BDF 20%	160.2 (2.2) ^b	-2.99 (0.18) ^b
PHB.BDF 40%	130.4 (4.7) ^a	-11.27 (0.80) ^a
PLA	148.3 (0.6) ^c	56.2 (1.75) ^c
PLA.BDF 10%	142.7 (2.1) ^b	35.9 (1.24) ^b
PLA.BDF 20%	140.9 (1.9) ^b	32.09 (0.72) ^b
PLA.BDF 40%	132.5 (1.9) ^a	12.27 (2.92) ^a

Different superscript letters (a-c) within each column indicate significant ($p < 0.05$) differences among mean observations for different polymeric formulations. Each value represents a mean of three replicates with the standard deviation in parentheses.

Figure captions

Figure 1. Release kinetics and mathematical modelling of the BDF from different polymeric films. Whereas a) PHBV.BDF 10, 20 and 40 w%, b) PHB.BDF 10, 20, and 40 w% and c) PLA.BDF 10, 20, and 40 w%. (Different superscript letters (a-d) beside each point indicate significant ($p < 0.05$) differences among mean observations). Furthermore, dots represent experimental values and lines represent mathematical models used for fitting.

Figure 2. FT-IR analysis of different PHBV films before and after release. Furthermore, AR means spectra recorded after release.

Figure 3. FT-IR analysis of different PHB films before and after release. Furthermore, AR means spectra recorded after release.

Figure 4. FT-IR analysis of different PLA films before and after release. Furthermore, AR means spectra recorded after release.

Figure 5. Antioxidant capacity of the active films a) PHBV films, b) PHB films, and c) PLA films.









