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1 **A comparative study on the effect of different reactive**
2 **compatibilizers on injection-molded pieces of bio-based**
3 **high-density polyethylene/polylactide blends**

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14
15
16 **Abstract.** The present study reports on the development of binary blends consisting of
17 bio-based high-density polyethylene (bio-HDPE) with polylactide (PLA), in the 5–20
18 wt% range, prepared by melt compounding and then shaped into pieces by injection
19 molding. In order to enhance the miscibility between the green polyolefin and the
20 biopolyester, different reactive compatibilizers were added during the melt blending
21 process, namely polyethylene-grafted maleic anhydride (PE-g-MA), poly(ethylene-*co*-
22 glycidyl methacrylate) (PE-*co*-GMA), maleinized linseed oil (MLO), and a combination
23 of MLO with dicumyl peroxide (DCP). Among the tested compatibilizers, the dual
24 addition of MLO and DCP provided the binary blend pieces with the most balanced
25 mechanical performance in terms of rigidity and impact strength as well as the highest
26 thermal stability. The fracture surface of the binary blend piece processed with MLO
27 and DCP revealed the formation of a continuous structure in which the dispersed PLA
28 phase was nearly no discerned in the bio-HDPE matrix. The resultant miscibility
29 improvement was ascribed to both the high solubility and plasticizing effect of MLO
30 on the PLA phase as well as the cross-linking effect of DCP on both biopolymers. The
31 latter effect was particularly related to the formation of macroradicals of each
32 biopolymer that, thereafter, led to the *in situ* formation of bio-HDPE-*co*-PLA
33 copolymers and also to the development of a partially cross-linked network in the
34 binary blend. As a result, cost-effective and fully bio-based polymer pieces with
35 improved mechanical strength, high toughness, and enhanced thermal resistance were
36 obtained.

37 **Keywords:** Green polyolefins, PLA, reactive extrusion, multi-functionalized
38 vegetable oils, peroxides, mechanical properties

40 1. INTRODUCTION

41
42 Current awareness of environmental issues related to the extensive use of plastics and
43 the increasing necessity of reducing the carbon footprint is generating a great interest
44 in the use of polymer materials derived from natural resources and with great capacity
45 to be recycled. This trend has significantly raised both the interest and use of bio-based
46 and biodegradable polymers, which are capable of decomposing in composting
47 conditions and show similar technical characteristics than their fossil-derived
48 counterparts.¹ Although the price and performance of most biopolymers are still far to
49 those of petrochemical polymers,² the development of either green composites^{3,4} or
50 biopolymer blends^{5,6} can certainly contribute to promote the use of biopolymers at
51 industrial scale.

52 The use of binary blends represents a cost-effective strategy to obtain a good
53 combination of physical properties and also to reduce the final cost of the biopolymers.
54 This consists of mixing two dissimilar biopolymers in order to obtain formulations
55 with intermediate or better performance than those of the neat biopolymers. In this
56 sense, on the one hand, bio-based polyethylene (bio-PE) combines natural origin with
57 the easy processability and optimal performance of polyolefins. In this sense, high-
58 density polyethylene (HDPE) is among the top five plastic materials in the world in
59 terms of volume, reaching 31.3 million tons in 2009.⁷ On the other hand, polylactide
60 (PLA) is currently the most used bio-based and biodegradable polyester. PLA is
61 obtained through the polycondensation reaction of lactides, the dimers that are, in
62 turn, obtained from the fermentation of sugars based on starch.⁸ Currently, PLA is
63 considered the front runner in the emerging market of bioplastics due to its good
64 balance between mechanical, thermal, and barrier properties, and its double
65 environmental advantage of being a bio-based and biodegradable material. For these
66 reasons, it is now widely used in 3D printing,⁹ biomedical applications,^{10,11} automotive
67 and textiles,¹² packaging,¹³ etc.

68 Recycling is an interesting solution to minimize plastic wastes but its main drawbacks
69 are related to collection and separation, particularly in the case of multilayers.
70 Polyolefins such as polyethylene (PE) and polypropylene (PP) are, with difference, the
71 most recycled polymers but sometimes, due to the difficulty in separating polymers,
72 they can be recycled with low amounts of other polymers (even immiscible) without
73 compromising their overall performance. As mentioned above, PLA is gaining interest
74 at industrial scale and, therefore, it is everyday more present in plastic wastes that can
75 be potentially subjected to recycling. As it is a relatively new polymer in plastic waste
76 streams (with a relatively low percentage in comparison to other polymers), separation
77 is still complex and expensive at this stage, so that, PLA could be present in low
78 amounts in recycled PE and PP streams, leading to complex blends. Polyolefins are
79 highly hydrophobic polymers (non-polar) while, in general, thermoplastic polyesters
80 are more hydrophilic (polar) due to the presence of ester groups and other oxygen-
81 based groups. This difference in polarity leads to a high difference between their
82 solubility parameters (δ). In fact, the δ value of PE is close to 16.0 MPa^{1/2} while PLA
83 shows a typical value of 20 MPa^{1/2}, resulting in a poor or lack of miscibility between
84 them.^{4,14-17}

85 The mixture of polymers with a dissimilar physical properties is widely considered as
86 an economic technique to produce plastic materials that have a desirable combination
87 of properties and may also have the ability to recycle or degrade after usage.^{18,19}
88 However, one of the main problems of the blends made of polyolefins and polyesters is

89 that they present total immiscibility. When mixed together, the resultant polymer
90 blends turn out to have a two-phase morphology in which the main component forms
91 a matrix and the minor component appears as the dispersion phase in the form of
92 spheres, platelets or even fibrils.²⁰ Unfortunately, immiscible mixtures are frequently
93 characterized by a poor adhesion between the phases and they generally require
94 compatibility for achieving improved performance.²¹

95 Two main methods can be applied to improve the miscibility between two or more
96 immiscible polymers, namely *ex situ* (non-reactive) or *in situ* (reactive)
97 compatibilization.²² *Ex situ* compatibilization is based on the use of a premade (block or
98 grafted) copolymer, being highly miscible with the blend components that are obtained
99 under careful design and synthesis. Usually, these copolymers possess dual
100 functionality, which means that a chain segment (with a particular chemical structure)
101 can interact with one polymer in the blend and the other segment chain (with other
102 chemical groups) can establish some interactions with the other polymer in the blend,
103 thus acting as a bridge between them. These tailor-made copolymers can reduce
104 particle size, increase morphological stability and interfacial adhesion, and improve
105 final mechanical properties.²³ Some copolymers have been specifically designed for
106 PLA^{24,25} or PE,^{22,26} providing good results as compatibilizers.²⁷ The second method to
107 improve the compatibility in polymer blends is the use of *in situ* (reactive)
108 compatibilization, the so-called reactive extrusion (REX), during the compounding of
109 the polymer formulation.^{28,29} *In situ* compatibilization is carried out by means of
110 polymers, oligomers, and additives containing multi-functional groups (e.g. anhydride,
111 epoxy, oxazoline, isocyanates, etc.) that are capable of reacting during the extrusion
112 process with the functional groups (e.g. hydroxyl and carboxyl terminal groups of
113 condensation polymers) to form new copolymers.^{29,30} REX is a straightforward and
114 cost-effective technique for polymer processing in which dicumyl peroxide (DCP), a
115 free radical initiator widely used in polymerization processes, can be additionally used
116 as an initiator and cross-linker.³¹ Indeed, DCP has been used to promote the
117 compatibilization of immiscible polymers in different polymer binary blends with
118 good results. For instance, Garcia-Garcia *et al.*³² improved the compatibility between
119 poly(3-hydrobutyrate) (PHB) and poly(ϵ -caprolactone) (PCL) by the addition of DCP.
120 Moreover, in a more sustainable context, derivatives of natural oils, such as acrylated,⁴
121 epoxidized³² or maleinized vegetable oils,^{4,33} can be used as reactive additives to
122 improve the properties of biopolymers and also to achieve compatibility in polymer
123 blends or even in green composites. Among them, epoxidized linseed oil and, more
124 lately, maleinized linseed oil (MLO) currently represent a sustainable solution in PLA-
125 based formulations.^{4,34-36}

126 Bio-based high-density polyethylene (bio-HDPE), also called "microbial" or "green"
127 HDPE, is a polyolefin produced by conventional polymerization of ethylene obtained
128 by catalytic dehydration of bioethanol.³⁷ Bio-HDPE has the same physical properties
129 than its counterpart petrochemical resin, particularly having a good mechanical
130 resistance, high ductility, and improved water resistance.³⁸ Injection-molded pieces of
131 bio-HDPE can be targeted to manufacture rigid plastic parts for packaging materials
132 and surfaces (e.g. cutting boards, kitchen utensils and countertops, and storage
133 containers).³⁹

134 The aim of this study was to prepare binary blends of bio-HDPE with PLA by melt
135 compounding in order to develop a cost-effective and fully renewable material with
136 high mechanical strength and rigidity but with still sufficient mechanical ductility. To

137 this end, this work explores the use of different reactive additives as compatibilizers,
138 such as copolymers and grafted polymers, multi-functionalized vegetable oils, and a
139 cross-linking agent, to enhance the miscibility between both biopolymers and obtain
140 the more balanced mechanical performance.

141

142 2. EXPERIMENTAL

143

144 2.1. Materials

145 Bio-HDPE was SHA7260, a grade for injection molding supplied by FKuR Kunststoff
146 GmbH (Willich, Germany) and manufactured by Braskem (São Paulo, Brazil). It has a
147 density of 0.955 g/cm³ and a melt flow index (MFI) of 20 g/10 min measured at 190 °C
148 and 2.16 kg. Its minimum bio-based content is 94%, as determined by the manufacturer
149 according to ASTM D6866. Commercial PLA Ingeo™ biopolymer 6201D was obtained
150 from NatureWorks (Minnetonka, MN, USA). This PLA grade has a density of 1.24
151 g/cm³ and a melt flow rate (MFR) of 15–30 g/10 min, measured at 210 °C and 2.16 kg,
152 which makes it suitable for injection molding.

153 Polyethylene-grafted maleic anhydride (PE-g-MA) and poly(ethylene-co-glycidyl
154 methacrylate) (PE-co-GMA), with reference numbers 456624 and 430862, respectively,
155 and MFI values of 5 g/10 min (190 °C/2.16 kg), were obtained from Sigma-Aldrich
156 S.A. (Madrid, Spain). These two PE-based copolymers were selected due to their dual
157 functionality: non-polar polyethylene segments and polar segments, either with maleic
158 anhydride (MA) or glycidyl methacrylate (GMA) groups, that can readily react with
159 the hydroxyl groups of the PLA end-chains. MLO, a maleinized vegetable oil from
160 linseed oil, was obtained from Vandeputte (Mouscron, Belgium) as VEOMER LIN. This
161 multi-functional reactive oil was selected due to its dual functionality since it contains
162 non-polar fatty acids and polar maleic anhydride-grafted fatty acids. The oil has a
163 viscosity of 1000 cP at 20 °C and an acid value of 105–130 mg potassium hydroxide
164 (KOH)/g. Finally, DCP, with 98% purity, was purchased from Sigma-Aldrich S.A.
165 (Madrid, Spain) and used to provide free radicals during the REX process. Figure 1
166 shows the chemical structure of each compatibilizer.

167

168 2.2. Preparation of biopolymer blends

169 REX was carried out in a co-rotating twin-screw extruder from Construcciones
170 Mecánicas Dupra, S.L. (Alicante, Spain). The speed of the screws, having a diameter of
171 25 mm with a ratio of length (L) to diameter (D), that is, L / D of 24, was set at 25 rpm
172 and the extrusion temperature profile, from the hopper to the die, was set as follows:
173 165–170–175–180 °C. All materials were fed through the main hopper, being previously
174 pre-homogenized in a zipper bag. These were extruded through a round die to
175 produce strands and pelletized using an air-knife unit. In all cases, residence time was
176 approximately 1 min. **Table 1** gathers the set of materials prepared during extrusion.
177 The additives were added as parts per hundred resin (phr) of biopolymer.

178 The compounded pellets were, thereafter, shaped into pieces by injection molding in a
179 Meteor 270/75 from Mateu & Solé (Barcelona, Spain). The temperature profile was 165

180 °C (hopper), 170 °C, 175 °C, and 180 °C (injection nozzle). A clamping force of 75 tons
181 was applied while the cavity filling and cooling time were set at 1 and 10 s,
182 respectively. Pieces with a thickness of 4 mm were produced. **Figure 2** shows a
183 schematic representation of the manufacturing process.

184

185 **2.3. Mechanical characterization**

186 The tensile tests were performed in a universal testing machine ELIB 50 of S.A.E.
187 Ibertest (Madrid, Spain) as recommended by ISO 527-1:2012. The tests were carried out
188 with a load cell of 5 kN and the loading speed was set to 40 mm/min.

189 The hardness measurements were done according to ISO 868:2003, using a Model 676-
190 D durometer (J. Bot Instruments S.A., Barcelona, Spain). The impact resistance was
191 measured using a 1-J Charpy pendulum test machine from Metrotex S.A. (San
192 Sebastián, Spain) in rectangular pieces with dimensions of 4x10x80 mm³ and a 0.25-mm
193 radius v-notch, according to the specifications of ISO 179-1:2010.

194 All samples were analyzed at room temperature, that is, 25 ° C, and at least 6 samples
195 of each material were tested and their values averaged.

196

197 **2.4. Morphological characterization**

198 The morphology of the fracture surfaces of the biopolymer pieces obtained from the
199 impact tests was observed by field emission scanning electron microscopy (FESEM) in
200 a ZEISS ULTRA 55 from Oxford Instruments (Abingdon, UK). Prior to placing the
201 samples in the vacuum chamber, the surfaces were sputtered with a gold-palladium
202 alloy in an EMITECH sputter coating SC7620 model from Quorum Technologies, Ltd.
203 (East Sussex, UK). An acceleration voltage of 2 kV was applied.

204

205 **2.5. Thermal characterization**

206 The main thermal transitions of the biopolymer pieces were obtained by differential
207 scanning calorimetry (DSC) in a Mettler-Toledo 821 calorimeter (Schwerzenbach,
208 Switzerland). An average sample weight of 5 to 7 mg was subjected to a thermal cycle
209 as follows: initial heating from 25 °C to 200 °C, cooling to -50 °C, and second heating to
210 300 °C, at a heating rate of 10 °C/min. All tests were performed under a nitrogen
211 atmosphere (66 mL/min) with standard sealed aluminum crucibles with a volume
212 capacity of 40 µL.

213 Thermogravimetric analysis (TGA) was carried out in a Mettler-Toledo TGA/SDTA
214 851 thermobalance (Schwerzenbach, Switzerland). Samples, with an average weight
215 between 5 and 7 mg, were placed in standard alumina crucibles (70 µL) and subjected
216 to a heating program from 30 °C to 700 °C at a heating rate of 20 °C/min in air
217 atmosphere.

218 All thermal tests were performed in triplicate.

219

220 **2.6. Thermomechanical characterization**

221 Dynamical mechanical thermal analysis (DMTA) was carried out in a DMA1 dynamic
222 analyzer from Mettler-Toledo (Schwerzenbach, Switzerland), working in single
223 cantilever flexural conditions. Samples with dimensions of 20x6x2.7 mm³ were
224 subjected to a temperature sweep from -160 °C to 100 °C at a constant heating rate of 2
225 °C/min. The selected frequency was 1 Hz while the maximum flexural deformation
226 was 10 µm.

227 The dimensional stability of the injection-molded pieces was estimated by
228 thermomechanical analysis (TMA) in a Q-400 thermoanalyzer from TA Instruments
229 (Newcastle, DE, USA) using rectangular samples of 10x10x4 mm³. A dynamic
230 temperature ramp was programmed from -160 °C to 100 °C, at a heating rate of 3
231 °C/min and a constant load of 0.02 N.

232 All thermomechanical tests were run in triplicate.

233

234 **3. RESULTS AND DISCUSSION**

235

236 **3.1. Mechanical properties**

237 The mechanical characterization of the injection-molded pieces made of bio-HDPE and
238 its blends with PLA provides relevant information in terms of the effect of the blend
239 composition and the tested additives as well as their most suitable applications. **Table**
240 **2** shows the values of tensile modulus (E_{tensile}), maximum tensile strength (σ_{max}),
241 elongation at break (ϵ_b) of the pieces obtained from the tensile tests. One can observe
242 that the neat bio-HDPE piece presented values of E_{tensile} and σ_{max} of 408.4 MPa and 21.6
243 MPa, respectively, while ϵ_b was 545.2%, indicating that the material was relatively rigid
244 and with a high ductility. The incorporation of PLA into bio-HDPE resulted in rigidity
245 increase of the pieces, that is, the E_{tensile} values varied from 492.9 MPa, for the piece
246 containing 5 wt% PLA, up to 563 MPa, for the piece with 20 wt% PLA. However, while
247 the σ_{max} was kept in the same range or even showed slightly higher values than the
248 neat bio-HDPE piece, that is, in the 21.5–23.5 MPa range, the ϵ_b values of the pieces
249 significantly decreased with the PLA content. For instance, the bio-HDPE/20PLA piece
250 showed a ϵ_b value of 54%, that is, approximately 10 times lower than that observed for
251 the neat bio-HDPE. The reduction induced in the ductile properties suggests a poor
252 stress transfer between the two biopolymer phases in which, more likely, the PLA
253 phase acted as a stress concentrator in the bio-HDPE matrix favoring the rupture of the
254 pieces.

255 The addition of the different compatibilizers was analyzed on the bio-HDPE/20PLA
256 pieces. It can be observed that the studied compatibilizers induced very dissimilar
257 effects on the mechanical properties of the binary blend pieces. In relation to the PE-
258 based compatibilizers, both PE-g-MA and PE-co-GMA delivered a similar
259 improvement in E_{tensile} , reaching values of approximately 570 MPa, and a slight
260 reduction in σ_{max} . In contrast, the addition of PE-g-MA slightly increased ϵ_b , reaching a

value of 57.7%, while PE-*co*-GMA induced a significant reduction in ductility down to a value of 34.4%. This suggests that the latter additive could produce certain cross-linking in the biopolymer blend. Similar results were obtained, for instance, by Abdolrasouli *et al.*⁴⁰ using PE-*g*-MA as compatibilizer in PLA/PE blends containing organoclays. In particular, it was observed that the PLA/PE/PE-*g*-MA 80/12/8 (wt/wt) blends increased ϵ_b around 30%, while the tensile strength properties remained almost constant in comparison to an unmodified PLA/PE blend. In this sense, it is worthy to note that the selected PE-based compatibilizers show dual functionality. On one hand, the hydrophobic PE blocks and, on the other hand, the highly polar and reactive MA and GMA groups. The PE blocks/segments can then interact with the bio-HDPE chains in the blend while both the MA and GMA groups can readily react/interact with the hydroxyl groups of PLA through esterification and etherification reactions, respectively. This way, the PE-based compatibilizer chains tended to place at the interface between the bio-HDPE and PLA phases thus acting as a bridge between the two immiscible phases. This partial compatibilization has been reported to yield improved miscibility and allows somewhat load transfer between both polymers in the blend, thus, overcoming (or minimizing) the negative effects of immiscibility.^{41,42}

In the case of MLO, the addition of the vegetable oil generated pieces with similar or slightly lower mechanical properties than the neat bio-HDPE/20PLA piece. This reduction in the mechanical strength has been previously related to the plasticizing effect of MLO on the PLA matrix, in which the multi-functionalized oil also produced an increase in ductility.^{4,35} However, the absence of improvement in the ϵ_b value of the here-described pieces suggests that the vegetable oil presented a low solubility and, thus, a poor effect on the bio-HDPE matrix. Interestingly, the combination of MLO and DCP resulted in more rigid injection-molded pieces, showing the highest $E_{tensile}$ value among the tested pieces, that is, 582 MPa, and the lowest ϵ_b value, that is, 23.2%. As similar to the PE-*co*-GMA-treated piece, it can be considered that the addition of the peroxide additive generated a cross-linked structure in the polymer blend. The cross-linking effect of DCP has been tested in different polymers, blends, and composites.⁴³⁻⁴⁶ Similar results were observed, for instance, by Sen-lin Yang *et al.*⁴⁷ where the DCP addition resulted in a cross-linking of the PLA structure, yielding a stiffened material with a higher $E_{tensile}$ and lower ϵ_b .

Table 2 also shows the values of Shore D hardness and impact strength of the biopolymer pieces. Similar to the tensile tests, the addition of PLA induced an increase in hardness and a reduction in toughness in comparison to the neat bio-HDPE piece. In particular, while the neat bio-HDPE piece presented a Shore D hardness of 61.8 and an impact-strength value of 3.77 kJ/m², the addition of PLA progressively increased hardness up to 67.4, while it decreased impact strength up to 1.70 kJ/m², both values for the bio-HDPE/20PLA piece. Similar to the tensile properties, the use of PE-*g*-MA slightly increased hardness but reduced impact strength. As opposite, PE-*co*-GMA produced pieces with similar hardness but a higher toughness. In particular, the impact-strength value increased to 2.01 kJ/m², that is, an increase of approximately 18%. For the MLO-containing piece, hardness was lower, that is, 58.8, while the impact strength was significantly increased, reaching a value of 3.96 kJ/m², representing an improvement close to 133%. This observation points to the fact that the multi-

functionalized oil was probably preferentially incorporated in the PLA-rich regions as a dispersed phase. A similar effect was previously observed for PLA pieces containing acrylated epoxidized soybean oil,⁴ in which the multi-functionalized oil was dispersed in the form of fine droplets contributing to increasing the impact-absorbed energy in a similar way as, for instance, polybutadiene rubbers do in high-impact polystyrene. This remarkable toughening effect was maintained for the injection-molded piece produced with MLO in combination to DCP, which also showed hardness values close to those of the neat bio-HDPE/20PLA.

Although the dual incorporation of DCP and MLO improved the impact strength of the bio-HDPE/20PLA piece it also resulted in a slight reduction of 0.25 kJ/m² with respect to the MLO-containing bio-HDPE/20PLA piece. This effect can be thus ascribed to the cross-linking effect of DPC on the binary blend, which resulted in a more interconnected network of biopolymer chains that increased the mechanical resistance of the pieces but also reduced its toughness. In this sense, it has been reported that DCP can be effectively applied as a reactive compatibilizer in polymers blends since it decomposes and acts as a free radical initiator.⁴² For instance, Garcia-Garcia *et al.*⁴⁸ prepared PHB and PCL blends compatibilized with DCP. It was observed that DCP not only promoted the formation of macroradicals of each biopolymer that, thereafter, led to the formation of *in situ* PHB-*co*-PCL copolymers that contributed to improving compatibilization and forming partially cross-linked networks in the blends, but also the PCL-rich domains could establish stronger interactions with the PHB polymer matrix. Hence, the use of DCP during the melt mixing of polymer blends can yield a series of grafted, branched, and/or cross-linked structures in polymer blends.⁴⁹

331

332 3.2. Morphological characterization

333 **Figure 3** includes the FESEM images of the fracture surfaces of the biopolymer pieces
334 after the impact tests. **Figure 3a**, corresponding to the neat bio-HDPE piece, shows a
335 fracture surface with a very irregular and rough appearance presenting the typical
336 cavernous formations of a polymer with a ductile behavior. Due to the low miscibility
337 between both biopolymers, one can observe in **Figures 3b to 3e** that PLA remained
338 incorporated into the bio-HDPE matrix as a dispersed phase in the form of micro-sized
339 spherical domains or droplets generating an “island-and-sea” morphology. The
340 absence of a co-continues phase morphology in the blends supports previous studies
341 indicating that, at the here-studied mixing ratios, these biopolymers are
342 thermodynamically immiscible.⁵⁰ Additionally, these droplets were larger as the
343 percentage of the added PLA was increased. In particular, the size of these droplets
344 ranged between 1–2 µm for the bio-HDPE/5PLA piece, 2–3 µm for the bio-
345 HDPE/10PLA piece, 3–5 µm for the bio-HDPE/15PLA piece, and 4–8 µm for the bio-
346 HDPE/20PLA piece. One can also observe the existence of a gap or a lack of continuity
347 between the PLA droplets and the bio-HDPE matrix, which was more noticeable in the
348 pieces with the highest PLA contents, shown in **Figures 3d and 3e**. In addition, the
349 fracture surfaces presented several holes, suggesting a phenomenon of phase
350 debonding after breakage. Both the presence of gaps and holes further indicates the
351 lack of compatibility between the two phases, therefore suggesting that the presence of

352 the PLA microdroplets acted as stress concentrators rather than a reinforcing element.
353 This would explain the above-described mechanical performance of the bio-
354 HDPE/PLA pieces, by which when the pieces are subjected to external stresses the
355 microdroplets are responsible for their loss of intrinsic ductility.

356 In relation to the effect of the different tested compatibilizers, one can observe that the
357 surface fracture of the piece treated with PE-g-MA, shown in **Figure 3f**, presented a
358 similar morphology than that of the neat bio-HDPE/20PLA piece. However, the mean
359 size of the PLA droplets was slightly lower, that is, 4-6 μm , and the number of voids
360 was also reduced. This reduction of the PLA domains was more evident in the case of
361 the pieces treated with PE-*co*-GMA, where the mean droplets size was in the 1-2 μm
362 range. Moreover, the gap at the interface between the two polymers was significantly
363 reduced. This suggests that a higher coalescence stabilization in the biopolymer blend
364 was successfully achieved due to a reduced surface tension between the phases. This
365 phenomenon would then explain the improved capacity of energy absorption observed
366 during the impact tests. A similar morphological effect was previously observed by
367 Wang *et al.*⁵¹ when PE-g-MA was used as a compatibilizer between HDPE and
368 poly(ethylene-*co*-vinyl alcohol) (EVOH). It was observed that the domain size of EVOH
369 decreased in the HDPE matrix when 10 phr PE-g-MA were used while the phase
370 boundaries disappeared as its content was higher than 20 phr. Similarly, Quiroz-
371 Castillo *et al.*⁵² showed positive results in low-density polyethylene (LDPE)/chitosan
372 blends due to the incorporation of 5 wt% PE-g-MAH.

373 In **Figure 3g** one can observe the surface fracture of the blend piece processed with
374 MLO. Noticeably, the droplets became larger, leading to the formation of big droplets
375 that also presented some stretching phenomenon along the bio-HDPE matrix. Further
376 observation at the droplet cross-sections revealed the presence of ultrathin enclosed
377 droplets or pores, which supports the above-described hypothesis that MLO was
378 mainly incorporated into the PLA phase. In any case, a large gap between the bio-
379 HDPE and PLA phases could be still discerned and, hence, the multi-functionalized
380 vegetable oil failed to yield compatibilization to the blend. Interestingly, the surface
381 fracture of the bio-HDPE/20PLA piece processed with MLO and DCP revealed the
382 presence of a continuous structure. Indeed, the dispersed PLA droplets were mostly no
383 longer discerned and it gave rise to the formation of a morphology in which the bio-
384 HDPE matrix fully covered the enclosed PLA regions. In particular, these PLA regions
385 showed a dendritic or branch-like shape, being produced during fracture as a result of
386 the high interaction between the two biopolymers. The fracture also produced a
387 rougher surface with certain plastic deformation where no evidence of phase
388 separation or pull-out of the inclusion phase after fracture was observed. This
389 morphological change can be attributed to both the *in situ* formation of bio-HDPE-*co*-
390 PLA copolymers to achieve compatibilization and the cross-linking effect of DCP,
391 above described during the mechanical analysis, which produced a fully
392 interconnected bio-HDPE/PLA structure. The previous work carried out by Ma *et al.*⁵³
393 showed that DCP is able to compatibilize PLA/PBAT blends by the formation of an *in-*
394 *situ* formed PLA-g-PBAT copolymer, reducing the size of the PBAT domains
395 embedded in the PLA matrix from 1.0 μm to 0.6 μm after addition of 0.1 wt% DCP. In
396 another work, Li *et al.*⁵⁴ observed that the addition of 0.5% DCP to polyamide
397 11/EVOH blends favored the formation of more fine spherical domains. Moreover,

398 large number of thinner and longer embedded flat-like structures of EVOH were
399 obtained when 1.5% DCP was added.

400

401 3.3. Thermal characterization

402 **Figure 4** shows the DSC curves during the second heating of the biopolymer pieces.
403 One can observe that the neat bio-HDPE presented a melting temperature (T_m) of 132.2 ± 1.5 °C.
404 The addition of PLA generated a second endothermic peak, related to the
405 melting of PLA, which was observed in the 160–180 °C range. For the bio-
406 HDPE/20PLA blend instance, this peak was centered at approximately at 169.6 ± 0.7
407 °C. The second peak intensity was relatively low though it was more noticeable at high
408 PLA contents, that is, 15 and 20 wt%. Additionally, it can be observed that the T_m
409 values of the bio-HDPE phase slightly decreased gradually with increasing the PLA
410 content, up to 131.4 ± 1.1 °C, for the bio-HDPE/20PLA blend. The melting enthalpies
411 were also lower in the blend formulations with higher PLA contents. In overall, the
412 thermal values remained almost constant, which confirmed the poor compatibility or
413 absence of miscibility between both biopolymers. A similar observation was previously
414 obtained in, for instance, PLA/PP blends.⁵⁵

415 With the incorporation of the different compatibilizers, some interesting changes in the
416 thermal properties of the injection-molded pieces could be observed. While the melting
417 profile of the blends remained nearly constant with the addition of both PE-g-MA and
418 PE-co-GMA, the use of MLO in combination with DCP produced both an increase in
419 the T_m value related to the bio-HDPE phase, that is, 134.5 ± 1.0 °C, and a decrease for
420 the PLA phase, that is, 167.2 ± 0.8 °C. This slight shift in the characteristic melting
421 profiles of HDPE and PLA can be related to the formation of some HDPE-g-PLA
422 copolymer chains due to the action of DCP, which can provide free radicals to attach
423 the HDPE chains, and MLO, which can react with the hydroxyl groups in PLA and also
424 provide plasticization. Although the change was not substantial, it gives some
425 evidence of the synergistic compatibilizing effect of DCP and MLO on the blends of
426 bio-HDPE with PLA. Similar findings were reported by, for instance, Lai *et al.*⁵⁶ in
427 binary blends of PLA with thermoplastic polyurethane (TPU) compatibilized with
428 aminosilane. A depression in the characteristic melting peak of PLA was attributed to a
429 lubrication provided by the compatibilized chains with a low molecular weight (M_w).
430 Although MLO, as similar to other vegetable oils, is able to plasticize PLA and then to
431 increase its free volume and reduce the biopolymer-biopolymer interactions,⁴ this
432 effect was not observed in the neat MLO-containing blend piece, suggesting that the
433 addition of DCP favored certain miscibility for the whole blend system. In any case, the
434 absence of significant melting peak shifts towards intermediate temperatures, in
435 between the melting peaks of each polymer in the blend, confirmed the presence of
436 two phases with different crystal types and therefore the absence of a fully miscible
437 structure.²²

438 In relation to thermal stability, **Figure 5** shows the TGA curves for the here-prepared
439 biopolymer pieces whereas **Table 3** summarizes the obtained values from the curves.
440 The neat bio-HDPE piece presented an onset degradation temperature, defined as the
441 temperature at which the material losses 5% of its mass ($T_{5\%}$), of 312.5 ± 1.7 °C. Its

442 degradation temperature (T_{deg}), determined at the temperature when the mass loss was
443 maximum, was 455.2 ± 1.5 °C. Additionally, the green polyolefin degraded in a single
444 stage, giving a residual mass of 0.3 ± 0.2 %. A similar thermal degradation profile has
445 been recently observed by Montanes *et al.*⁵⁷ for bio-HDPE. Interestingly, it can be seen
446 that the incorporation of PLA positively delayed the degradation onset of bio-HDPE,
447 up to values in the range of 324–329 °C, but it also reduced the values of T_{deg} . In
448 particular, the TGA curves presented two main weight losses. The first one occurred
449 from 320 °C to 390 °C, which can be related to the initial thermal decomposition of bio-
450 HDPE and mainly to the whole thermal degradation of the PLA phase. The second one
451 was observed in the 400–510 °C range, which can be ascribed to the chain-scission
452 process of bio-HDPE. In this sense, Garcia-Campo *et al.*⁵⁸ has recently analyzed the
453 thermal degradation of PLA, showing that the thermal decomposition of the
454 biopolyester occurs in one single step, in the 300–400 °C range, with $T_{5\%}$ and T_{deg}
455 values of 328.5 °C and 368.5 °C, respectively.

456 While the incorporation of both PE-g-MA and PE-co-GMA compatibilizers induced no
457 changes in the thermal stability of the bio-HDPE/20PLA pieces, the MLO-containing
458 pieces presented a slight improvement. In particular, the values of $T_{5\%}$ increased from
459 324.9 ± 1.6 °C, for the neat the bio-HDPE/20PLA piece, to 332.9 ± 2.1 °C and 338.9 ± 1.4
460 °C, for the pieces containing MLO and MLO with DPC, respectively. In the case of T_{deg} ,
461 the first degradation peak was also delayed from 358.1 ± 2.0 °C, for the neat the bio-
462 HDPE/20PLA piece, to 360.9 ± 2.1 °C and 365.1 ± 1.9 °C, for the pieces containing MLO
463 and MLO with DPC, respectively. An increase in thermal stability by the incorporation
464 of multi-functionalized vegetable oils has already been reported in some of our
465 previous works,^{4,34} which was related to the development of a macromolecule with a
466 higher M_w . In the case of the piece treated with MLO and DCP, the thermal stability
467 improvement can be ascribed to the partial cross-linking achieved in the blend. In this
468 sense, it has been reported that the thermal stability of biopolymers can be improved,
469 to a certain extent, with the addition DCP.^{32,59} In relation to the residual mass, it can be
470 seen that, in all cases, small residual amounts in the 0.1–0.5% range were produced.

471

472 3.4. Thermomechanical characterization

473 **Figure 6a** presents the evolution of the storage module (G') in the here-developed bio-
474 HDPE/PLA pieces from -150 °C to 100 °C. In relation to the neat bio-HDPE piece, a
475 sharp decrease of G' was produced up to -100 °C, which can be related to the glass-to-
476 rubber transition of the green polyolefin. Then, it progressively decreased as the test
477 temperature increased due to a softening effect of the bio-HDPE matrix. The
478 incorporation of PLA into the bio-HDPE matrix induced a slight decrease in G' , which
479 was more pronounced as the percentage of PLA increased. In particular, at -150 °C, it
480 decreased from 2493 MPa, for the neat bio-HDPE piece, to 2140 MPa, for the bio-
481 HDPE/20PLA piece. This reduction was observed up to temperatures close to 0 °C,
482 which supposed a decrease in the overall rigidity of the material. Similar to other
483 physical properties, the addition of both PE-g-MA and PE-co-GMA resulted in a similar
484 thermomechanical profile whereas the MLO induced some relevant changes. In the
485 case of the neat MLO-treated bio-HDPE/PLA piece, lower G' values were observed in
486 the whole temperature range. This reduction has been ascribed to the intrinsic

487 plasticizing effect provided by MLO on polyesters.⁴ In any case, the G' reduction was
488 relatively low, indicating that the oil mainly plasticized the dispersed PLA phase, as
489 described above during the morphological analysis. The combined use of MLO and
490 DCP provided, in a similar way to the mechanical and thermal properties described
491 above, the highest rigidity increase. This change was mainly seen in the temperature
492 range from -100 °C to -25 °C, while at higher temperatures all pieces presented a similar
493 thermomechanical performance. For instance, at -25 °C, the G' value increased from
494 1229.5 MPa, for the neat bio-HDPE/20PLA piece, to 1369.6 MPa, for the same piece
495 processed with MLO and DCP.

496 **Figure 6b** shows the evolution of the damping factor ($\tan \delta$) in the bio-HDPE/PLA
497 pieces. The peak located between -112 °C and -116 °C in the bio-HDPE piece sample
498 corresponds to alpha (α)-relaxation of the green polyolefin, which is related to its glass
499 transition temperature (T_g). The PLA blending generated a second peak, seen in the
500 65–75 °C range, which can be similarly related to the α -relaxation of PLA. The addition
501 of the compatibilizers induced almost no change in the α -relaxation peak of bio-HDPE,
502 while they slightly reduced that of PLA. In the case of PE-g-MA and PE-co-GMA, this
503 reduction was of only 3–4 °C while the MLO and MLO combined with DCP reduced
504 approximately by 7 and 11 °C, respectively, the α -relaxation peak of PLA. This
505 thermomechanical change can be ascribed to the above-mentioned process of
506 plasticization of the PLA phase by MLO while, particularly for the piece also treated
507 with DCP, this further confirms the improved compatibilization by the peroxide.
508 Indeed, the study of T_g gives an indication of the level of miscibility in polymer blends.
509 Briefly, thermodynamically immiscible blends show different distinguishable T_g
510 values, partially miscible blends have tendency to shift the T_g value of one component
511 toward that of the other, and blends made of two polymers that constitute a completely
512 miscible blend present a single T_g .²² Therefore, the here-observed shift of T_g for the PLA
513 phase with the combined used of MLO and DCP further supports the partial
514 miscibility with bio-HDPE in the binary blends. Similar results were obtained by Wang
515 *et al.*⁶⁰ for thermoplastic dry starch (DTPS) blends with PLA compatibilized by MA in
516 the presence of DCP. In particular, T_g of DTPS shifted to a higher temperature, while
517 PLA's T_g moved to a lower temperature.

518 In addition to DMTA, the dimensional stability was evaluated by TMA. To this end,
519 the coefficient of linear thermal expansion (CLTE) was studied in the injection-molded
520 pieces and the obtained results are summarized in **Table 4**. Below T_g of bio-HDPE, that
521 is, -110 °C, one can observe that the PLA addition to the mixture slightly reduced the
522 CLTE values, making the pieces somewhat stiffer in their glassy region. In particular, it
523 was decreased from $112.7 \pm 0.3 \mu\text{m/m}^\circ\text{C}$, for the neat bio-HDPE piece, to 107.6 ± 1.2
524 $\mu\text{m/m}^\circ\text{C}$, for the bio-HDPE/20PLA piece. The incorporation of the different
525 compatibilizers further enhanced the reduction of the CLTE values, reaching the lowest
526 CLTE value for the piece processed with MLO and DCP, that is, $90.6 \pm 1.3 \mu\text{m/m}^\circ\text{C}$. As
527 the temperature was increased during the test, the CLTE values also increased. In the
528 temperature range between both T_g s, that is, from -110 °C to 70 °C, the same trend was
529 observed. The addition of PLA reduced the CLTE values from $134.0 \pm 0.4 \mu\text{m/m}^\circ\text{C}$, for
530 the neat bio-HDPE piece, to $94.3 \pm 1.1 \mu\text{m/m}^\circ\text{C}$, for the bio-HDPE/20PLA piece.
531 However, only the piece treated with MLO in combination with DCP showed an
532 improvement in the thermomechanical response, having a value of $85.8 \pm 1.2 \mu\text{m/m}^\circ\text{C}$.

533 The greatest thermomechanical changes were observed at temperatures higher than 70
534 °C, that is, above T_g of PLA. While the neat bio-HDPE piece showed a CLTE value of
535 $465.3 \pm 0.6 \mu\text{m/m}^\circ\text{C}$, the addition of PLA positively reduced this values up to $342.1 \pm$
536 $0.96 \mu\text{m/m}^\circ\text{C}$, for the piece containing 20 wt% PLA. This implies a lower expansion
537 with temperature, thus improving the service conditions of the injection-molded
538 pieces. Although the addition of all compatibilizers increased the CLTE values of the
539 bio-HDPE/20 PLA pieces, the combined use of MLO and DCP again successfully kept
540 this value in the same order of magnitude, that is, $359.4 \pm 1.1 \mu\text{m/m}^\circ\text{C}$. It is worthy to
541 mention the high increase observed for the MLO-treated piece, reaching a CLTE value
542 of $525.1 \pm 1.0 \mu\text{m/m}^\circ\text{C}$. This further supports the plasticization produced in the
543 dispersed PLA phase, as described in detail in our previous studies.^{4,6,61}

544

545 4. CONCLUSIONS

546 The present study describes the preparation by melt compounding and subsequent
547 injection molding of binary blend pieces of bio-HDPE/PLA, at PLA contents from 5
548 wt% to 20 wt%, with the aim to develop a cost-effective and fully renewable plastic
549 articles with high mechanical strength and rigidity but with still sufficient mechanical
550 ductility. Whereas the incorporation of PLA into bio-HDPE resulted in an increase of
551 the mechanical strength of the pieces, their toughness significantly decreased with the
552 PLA content. The reduction observed in the ductile properties suggested a poor stress
553 transfer between the two biopolymer phases, due their lack of compatibility, in which
554 the dispersed PLA phase potentially acted as a stress concentrator in the bio-HDPE
555 matrix favoring the piece rupture. The low of miscibility, at the here-studied mixing
556 ratios, between both biopolymers was confirmed by morphological analysis of the
557 fracture surfaces of pieces after the impact tests. In particular, it was observed that PLA
558 remained mainly incorporated into the bio-HDPE matrix as a dispersed phase in the
559 form of micro-sized spherical domains or droplets to generate an “island-and-sea”
560 morphology. The thermal and thermomechanical studies carried out on the
561 biopolymer pieces further confirmed the poor compatibility or absence of miscibility
562 between bio-HDPE and PLA.

563

564 In order to increase miscibility and, thus, the mechanical and thermal performance of
565 the pieces, different reactive compatibilizers were tested on the blend pieces of bio-
566 HDPE with 20 wt% PLA, that is, bio-HDPE/20PLA. In particular, it was explored the
567 use of a grafted polymer, that is, PE-g-MA, a copolymer, that is, PE-*co*-GMA, a multi-
568 functionalized vegetable oils, that is, MLO, and a combination of MLO with a peroxide,
569 that is, DCP. The obtained results showed that the addition of either PE-g-MA or PE-*co*-
570 GMA induced a low improvement on the physical performance of the pieces since
571 these additives were not able to interact with both biopolymers and the binary blend
572 pieces still presented a marked phase separation. In relation to MLO, it was observed
573 that the multi-functionalized vegetable oil was mainly solubilized in the dispersed PLA
574 phase, which became highly plasticized so that it induced an overall enhancement of
575 the ductile properties in the binary blend pieces. Interestingly, the optimal
576 performance was attained for the binary blend piece simultaneously treated with MLO
577 and DCP, which presented the highest modulus, that is, 582 MPa, and also a relatively

578 high value of impact strength, that is, 3.71 kJ/m². The fracture surface of the bio-
579 HDPE/20PLA piece processed with MLO and DCP revealed the presence of a
580 continuous structure where the dispersed MLO-containing PLA droplets were mostly
581 no longer discerned and the bio-HDPE matrix fully covered the enclosed PLA regions.
582 This morphological change was attributed to the cross-linking effect of DCP, which
583 resulted in a more polymer interconnected network. The latter effect was related to the
584 formation of macroradicals of each biopolymer that, thereafter, led to the *in situ*
585 formation of bio-HDPE-*co*-PLA copolymers and also to the development of a partially
586 cross-linked network in the blend. Furthermore, the combined use of both
587 compatibilizers yielded a thermal stability increase of up to 14 °C.

588

589 It can be concluded that the combination of multi-functionalized vegetable oils and
590 peroxides represents an attractive strategy to enhance the miscibility between green
591 polyolefins and biopolymers and it can potentially contribute to the development of
592 sustainable polymer technologies. The here-obtained injection-molded pieces made of
593 bio-HDPE with up to 20 wt% PLA present higher mechanical resistance and similar
594 impact strength than those of neat bio-HDPE. These pieces, which are fully bio-based,
595 can be then regarded as great candidates for being used in sustainable rigid packaging.
596 Potential uses include, for instance, rigid packaging articles such as food trays and lids,
597 kitchen utensils and countertops, and storage containers, or surfaces such as cutting
598 boards.

599

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698

699 **Figure Captions**

700 **Figure 1.** Chemical structure of the different compatibilizers used in this work.

701 **Figure 2.** Schematic representation of the manufacturing process of the injection-
702 molded pieces of bio-based high-density polyethylene (bio-HDPE)/polylactide (PLA)
703 blends.

704 **Figure 3.** Field emission scanning electron microscopy (FESEM) images, taken at 1000 \times ,
705 of the surface fractures of the injection-molded pieces of: a) Neat bio-based high-
706 density polyethylene (bio-HDPE); b) Bio-HDPE/5 polylactide (PLA); c) Bio-
707 HDPE/10PLA; d) Bio-HDPE/15PLA; e) Bio-HDPE/20PLA; f) Bio-HDPE/20PLA +
708 polyethylene-grafted maleic anhydride (PE-g-MA); g) Bio-HDPE/20PLA +
709 poly(ethylene-co-glycidyl methacrylate) (PE-co-GMA); h) Bio-HDPE/20PLA +
710 maleinized linseed oil (MLO); i) Bio-HDPE/20PLA+MLO + dicumyl peroxide (DCP).
711 Scale markers of 20 μm .

712 **Figure 4.** Differential scanning calorimetry (DSC) curves of the injection-molded pieces
713 of bio-based high-density polyethylene (bio-HDPE) blended with different percentages
714 of polylactide (PLA) and compatibilized with polyethylene-grafted maleic anhydride
715 (PE-g-MA), poly(ethylene-co-glycidyl methacrylate) (PE-co-GMA), maleinized linseed
716 oil (MLO), and dicumyl peroxide (DCP).

717 **Figure 5.** Thermogravimetric analysis (TGA) curves of the injection-molded pieces of
718 bio-based high-density polyethylene (bio-HDPE) blended with different percentages of
719 polylactide (PLA) and compatibilized with polyethylene-grafted maleic anhydride (PE-
720 g-MA), poly(ethylene-co-glycidyl methacrylate) (PE-co-GMA), maleinized linseed oil
721 (MLO), and dicumyl peroxide (DCP): a) Weight loss and b) First derivate.

722 **Figure 6.** Dynamical mechanical thermal analysis (DMTA) curves of the injection-
723 molded pieces of bio-based high-density polyethylene (bio-HDPE) blended with
724 different percentages of polylactide (PLA) and compatibilized with polyethylene-
725 grafted maleic anhydride (PE-g-MA), poly(ethylene-co-glycidyl methacrylate) (PE-co-
726 GMA), maleinized linseed oil (MLO), and dicumyl peroxide (DCP): a) Storage
727 modulus (G') and b) damping factor ($\tan \delta$).

728

729 **Tables**

730 **Table 1.** Summary of compositions according to the weight content (wt%) of bio-based
 731 high-density polyethylene (bio-HDPE) and polylactide (PLA) in which polyethylene-
 732 grafted maleic anhydride (PE-g-MA), poly(ethylene-*co*-glycidyl methacrylate) (PE-*co*-
 733 GMA), maleinized linseed oil (MLO), and dicumyl peroxide (DCP) were added as
 734 parts per hundred resin (phr) of biopolymer blend.

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Sample	Bio-HDPE (wt%)	PLA (wt%)	PE-g-MA (phr)	PE- <i>co</i> -GMA (phr)	MLO (phr)	DCP (phr)
Bio-HDPE	100	0	0	0	0	0
Bio-HDPE/5PLA	95	5	0	0	0	0
Bio-HDPE/10PLA	90	10	0	0	0	0
Bio-HDPE/15PLA	85	15	0	0	0	0
Bio-HDPE/20PLA	80	20	0	0	0	0
Bio-HDPE/20PLA+PE- <i>g</i> -MA	80	20	3	0	0	0
Bio-HDPE/20PLA+PE- <i>co</i> -GMA	80	20	0	3	0	0
Bio-HDPE/20PLA+MLO	80	20	0	0	5	0
Bio-HDPE/20PLA+MLO+DCP	80	20	0	0	5	1

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737 **Table 2.** Mechanical properties in terms of tensile modulus ($E_{tensile}$), maximum tensile
 738 strength (σ_{max}), elongation at break (ϵ_b), Shore D hardness, and impact strength of the
 739 injection-molded pieces of bio-based high-density polyethylene (bio-HDPE) blended
 740 with different percentages of polylactide (PLA) and compatibilized with polyethylene-
 741 grafted maleic anhydride (PE-g-MA), poly(ethylene-*co*-glycidyl methacrylate) (PE-*co*-
 742 GMA), maleinized linseed oil (MLO), and dicumyl peroxide (DCP).

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Sample	$E_{tensile}$ (MPa)	σ_{max} (MPa)	ϵ_b (%)	Shore D hardness	Impact strength (kJ/m ²)
Bio-HDPE	408.4 ± 16.6	21.6 ± 0.4	545.2 ± 56.1	61.8 ± 0.8	3.77 ± 0.2
Bio-HDPE/5PLA	492.9 ± 11.1	21.7 ± 0.2	499.0 ± 74.5	62.0 ± 0.7	2.83 ± 0.2
Bio-HDPE/10PLA	500.0 ± 9.10	21.5 ± 0.2	253.2 ± 35.8	63.2 ± 0.8	1.88 ± 0.2
Bio-HDPE/15PLA	538.6 ± 6.34	22.2 ± 0.1	122.4 ± 6.73	66.2 ± 0.8	1.76 ± 0.2
Bio-HDPE/20PLA	563.0 ± 10.3	23.2 ± 0.3	54.0 ± 6.09	67.4 ± 1.1	1.70 ± 0.2
Bio-HDPE/20PLA+PE- <i>g</i> -MA	568.1 ± 8.84	22.7 ± 0.2	57.6 ± 4.33	68.0 ± 0.7	1.57 ± 0.2
Bio-HDPE/20PLA+PE- <i>co</i> -GMA	570.1 ± 6.38	22.1 ± 0.1	34.4 ± 4.28	67.5 ± 0.9	2.01 ± 0.3
Bio-HDPE/20PLA+MLO	496.1 ± 17.4	18.9 ± 0.2	50.5 ± 2.71	58.8 ± 1.5	3.96 ± 0.3
Bio-HDPE/20PLA+MLO+DCP	582.0 ± 6.07	22.0 ± 0.2	23.2 ± 1.16	65.8 ± 0.8	3.71 ± 0.5

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745 **Table 3.** Thermal properties in terms of onset degradation temperature ($T_{5\%}$),
 746 degradation temperature (T_{deg}), and residual mass at 700 °C of the injection-molded
 747 pieces of bio-based high-density polyethylene (bio-HDPE) blended with different
 748 percentages of polylactide (PLA) and compatibilized with polyethylene-grafted maleic
 749 anhydride (PE-g-MA), poly(ethylene-*co*-glycidyl methacrylate) (PE-*co*-GMA),
 750 maleinized linseed oil (MLO), and dicumyl peroxide (DCP).

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Sample	$T_{5\%}$ (°C)	$T_{deg\ 1}$ (°C)	$T_{deg\ 2}$ (°C)	Residual mass (%)
Bio-HDPE	312.5 ± 1.7	-	455.2 ± 1.5	0.2 ± 0.3
Bio-HDPE/5PLA	324.1 ± 1.4	359.5 ± 1.6	466.5 ± 1.8	0.3 ± 0.2
Bio-HDPE/10PLA	327.2 ± 1.8	356.2 ± 1.8	470.9 ± 1.5	0.2 ± 0.3
Bio-HDPE/15PLA	328.9 ± 1.5	355.2 ± 1.7	466.5 ± 1.6	0.3 ± 0.2
Bio-HDPE/20PLA	324.9 ± 1.6	358.1 ± 2.0	465.1 ± 1.9	0.1 ± 0.1
Bio-HDPE/20PLA+PE-g-MA	329.6 ± 1.9	356.6 ± 1.9	465.1 ± 1.4	0.3 ± 0.2
Bio-HDPE/20PLA+PE- <i>co</i> -GMA	327.3 ± 1.7	356.6 ± 1.7	445.2 ± 1.8	0.4 ± 0.1
Bio-HDPE/20PLA+MLO	332.9 ± 2.1	360.9 ± 2.1	453.7 ± 1.9	0.3 ± 0.2
Bio-HDPE/20PLA+MLO+DCP	338.9 ± 1.4	365.1 ± 1.9	465.1 ± 2.0	0.5 ± 0.3

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753 **Table 4.** Coefficients of linear thermal expansion (CLTE) of the injection-molded pieces
 754 of bio-based high-density polyethylene (bio-HDPE) blended with different percentages
 755 of polylactide (PLA) and compatibilized with polyethylene-grafted maleic anhydride
 756 (PE-g-MA), poly(ethylene-co-glycidyl methacrylate) (PE-co-GMA), maleinized linseed
 757 oil (MLO), and dicumyl peroxide (DCP).

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Sample	CLTE ($\mu\text{m}/\text{m } ^\circ\text{C}$)		
	$T < -110 \text{ } ^\circ\text{C}$	$-110 \text{ } ^\circ\text{C} \geq T \leq 70 \text{ } ^\circ\text{C}$	$T > 70 \text{ } ^\circ\text{C}$
Bio-HDPE	112.7 ± 0.3	134.0 ± 0.4	465.3 ± 0.6
Bio-HDPE/5PLA	110.7 ± 0.8	103.9 ± 0.6	457.2 ± 0.9
Bio-HDPE/10PLA	107.3 ± 1.3	110.2 ± 0.9	408.9 ± 0.5
Bio-HDPE/15PLA	109.2 ± 0.9	98.2 ± 0.7	408.7 ± 0.6
Bio-HDPE/20PLA	107.6 ± 1.2	94.3 ± 1.1	342.1 ± 0.9
Bio-HDPE/20PLA+PE-g-MA	109.5 ± 0.9	101.7 ± 0.8	356.8 ± 1.5
Bio-HDPE/20PLA+PE-co-GMA	101.2 ± 1.1	101.3 ± 0.9	499.2 ± 1.1
Bio-HDPE/20PLA+MLO	99.6 ± 0.9	102.1 ± 1.3	525.1 ± 1.0
Bio-HDPE/20PLA+MLO+DCP	90.6 ± 1.3	85.8 ± 1.2	359.4 ± 1.1

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