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

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

**Keywords:** Green polyolefins, PLA, reactive extrusion, multi-functionalized 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.<sup>1</sup> Although the price and performance of most biopolymers are still far to  
49 those of petrochemical polymers,<sup>2</sup> the development of either green composites<sup>3,4</sup> or  
50 biopolymer blends<sup>5,6</sup> 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.<sup>7</sup> 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.<sup>8</sup> 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,<sup>9</sup> biomedical applications,<sup>10,11</sup> automotive  
67 and textiles,<sup>12</sup> packaging,<sup>13</sup> 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 ( $\delta$ ). In fact, the  $\delta$  value of PE is close to 16.0 MPa<sup>1/2</sup> while PLA  
83 shows a typical value of 20 MPa<sup>1/2</sup>, resulting in a poor or lack of miscibility between  
84 them.<sup>4,14-17</sup>

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.<sup>18,19</sup>  
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.<sup>20</sup> Unfortunately, immiscible mixtures are frequently  
93 characterized by a poor adhesion between the phases and they generally require  
94 compatibility for achieving improved performance.<sup>21</sup>

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.<sup>22</sup> *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.<sup>23</sup> Some copolymers have been specifically designed for  
106 PLA<sup>24,25</sup> or PE,<sup>22,26</sup> providing good results as compatibilizers.<sup>27</sup> 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.<sup>28,29</sup> *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.<sup>29,30</sup> 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.<sup>31</sup> 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.*<sup>32</sup> improved the compatibility between  
119 poly(3-hydrobutyrate) (PHB) and poly( $\epsilon$ -caprolactone) (PCL) by the addition of DCP.  
120 Moreover, in a more sustainable context, derivatives of natural oils, such as acrylated,<sup>4</sup>  
121 epoxidized<sup>32</sup> or maleinized vegetable oils,<sup>4,33</sup> 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.<sup>4,34-36</sup>

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.<sup>37</sup> 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.<sup>38</sup> 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).<sup>39</sup>

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/cm<sup>3</sup> 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/cm<sup>3</sup> 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 Metrotec S.A. (San  
192 Sebastián, Spain) in rectangular pieces with dimensions of 4x10x80 mm<sup>3</sup> 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 mm<sup>3</sup> 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 mm<sup>3</sup>. 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 ( $E_{\text{tensile}}$ ), maximum tensile strength ( $\sigma_{\text{max}}$ ),  
241 elongation at break ( $\epsilon_b$ ) of the pieces obtained from the tensile tests. One can observe  
242 that the neat bio-HDPE piece presented values of  $E_{\text{tensile}}$  and  $\sigma_{\text{max}}$  of 408.4 MPa and 21.6  
243 MPa, respectively, while  $\epsilon_b$  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  $E_{\text{tensile}}$  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  $\sigma_{\text{max}}$  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  $\epsilon_b$  values of the pieces  
249 significantly decreased with the PLA content. For instance, the bio-HDPE/20PLA piece  
250 showed a  $\epsilon_b$  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  $E_{\text{tensile}}$ , reaching values of approximately 570 MPa, and a slight  
260 reduction in  $\sigma_{\text{max}}$ . In contrast, the addition of PE-g-MA slightly increased  $\epsilon_b$ , reaching a

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

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

294 **Table 2** also shows the values of Shore D hardness and impact strength of the  
295 biopolymer pieces. Similar to the tensile tests, the addition of PLA induced an increase  
296 in hardness and a reduction in toughness in comparison to the neat bio-HDPE piece. In  
297 particular, while the neat bio-HDPE piece presented a Shore D hardness of 61.8 and an  
298 impact-strength value of 3.77 kJ/m<sup>2</sup>, the addition of PLA progressively increased  
299 hardness up to 67.4, while it decreased impact strength up to 1.70 kJ/m<sup>2</sup>, both values  
300 for the bio-HDPE/20PLA piece. Similar to the tensile properties, the use of PE-g-MA  
301 slightly increased hardness but reduced impact strength. As opposite, PE-co-GMA  
302 produced pieces with similar hardness but a higher toughness. In particular, the  
303 impact-strength value increased to 2.01 kJ/m<sup>2</sup>, that is, an increase of approximately  
304 18%. For the MLO-containing piece, hardness was lower, that is, 58.8, while the impact  
305 strength was significantly increased, reaching a value of 3.96 kJ/m<sup>2</sup>, representing an  
306 improvement close to 133%. This observation points to the fact that the multi-



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

315 Although the dual incorporation of DCP and MLO improved the impact strength of  
316 the bio-HDPE/20PLA piece it also resulted in a slight reduction of 0.25 kJ/m<sup>2</sup> with  
317 respect to the MLO-containing bio-HDPE/20PLA piece. This effect can be thus  
318 ascribed to the cross-linking effect of DPC on the binary blend, which resulted in a  
319 more interconnected network of biopolymer chains that increased the mechanical  
320 resistance of the pieces but also reduced its toughness. In this sense, it has been  
321 reported that DCP can be effectively applied as a reactive compatibilizer in polymers  
322 blends since it decomposes and acts as a free radical initiator.<sup>42</sup> For instance, Garcia-  
323 Garcia *et al.*<sup>48</sup> prepared PHB and PCL blends compatibilized with DCP. It was observed  
324 that DCP not only promoted the formation of macroradicals of each biopolymer that,  
325 thereafter, led to the formation of *in situ* PHB-*co*-PCL copolymers that contributed to  
326 improving compatibilization and forming partially cross-linked networks in the  
327 blends, but also the PCL-rich domains could establish stronger interactions with the  
328 PHB polymer matrix. Hence, the use of DCP during the melt mixing of polymer blends  
329 can yield a series of grafted, branched, and/or cross-linked structures in polymer  
330 blends.<sup>49</sup>

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.<sup>50</sup> 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  $\mu\text{m}$ , 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  $\mu\text{m}$   
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.*<sup>51</sup> 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.*<sup>52</sup> 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.*<sup>53</sup>  
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  $\mu\text{m}$  to 0.6  $\mu\text{m}$  after addition of 0.1 wt% DCP. In  
396 another work, Li *et al.*<sup>54</sup> 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  $132.2$   
404  $\pm 1.5$  °C. 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  $169.6 \pm 0.7$   
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  $131.4 \pm 1.1$  °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.<sup>55</sup>

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,  $134.5 \pm 1.0$  °C, and a decrease for  
420 the PLA phase, that is,  $167.2 \pm 0.8$  °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.*<sup>56</sup> 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,<sup>4</sup> 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.<sup>22</sup>

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  $312.5 \pm 1.7$  °C. Its

442 degradation temperature ( $T_{deg}$ ), determined at the temperature when the mass loss was  
443 maximum, was  $455.2 \pm 1.5$  °C. Additionally, the green polyolefin degraded in a single  
444 stage, giving a residual mass of  $0.3 \pm 0.2$  %. A similar thermal degradation profile has  
445 been recently observed by Montanes *et al.*<sup>57</sup> 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.*<sup>58</sup> 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  $324.9 \pm 1.6$  °C, for the neat the bio-HDPE/20PLA piece, to  $332.9 \pm 2.1$  °C and  $338.9 \pm 1.4$   
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  $358.1 \pm 2.0$  °C, for the neat the bio-  
462 HDPE/20PLA piece, to  $360.9 \pm 2.1$  °C and  $365.1 \pm 1.9$  °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,<sup>4,34</sup> 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.<sup>32,59</sup> 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.<sup>4</sup> 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 ( $\alpha$ )-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  $\alpha$ -relaxation of PLA. The addition  
501 of the compatibilizers induced almost no change in the  $\alpha$ -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  $\alpha$ -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  $T_g$ .<sup>22</sup> 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.*<sup>60</sup> for thermoplastic dry starch (DTSP) blends with PLA compatibilized by MA in  
516 the presence of DCP. In particular,  $T_g$  of DTSP 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  $112.7 \pm 0.3 \mu\text{m}/\text{m}^\circ\text{C}$ , for the neat bio-HDPE piece, to  $107.6 \pm 1.2$   
524  $\mu\text{m}/\text{m}^\circ\text{C}$ , 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,  $90.6 \pm 1.3 \mu\text{m}/\text{m}^\circ\text{C}$ . 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  $134.0 \pm 0.4 \mu\text{m}/\text{m}^\circ\text{C}$ , for  
530 the neat bio-HDPE piece, to  $94.3 \pm 1.1 \mu\text{m}/\text{m}^\circ\text{C}$ , 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  $85.8 \pm 1.2 \mu\text{m}/\text{m}^\circ\text{C}$ .



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  $465.3 \pm 0.6 \mu\text{m}/\text{m}^\circ\text{C}$ , the addition of PLA positively reduced this values up to  $342.1 \pm$   
536  $0.96 \mu\text{m}/\text{m}^\circ\text{C}$ , 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,  $359.4 \pm 1.1 \mu\text{m}/\text{m}^\circ\text{C}$ . It is worthy to  
541 mention the high increase observed for the MLO-treated piece, reaching a CLTE value  
542 of  $525.1 \pm 1.0 \mu\text{m}/\text{m}^\circ\text{C}$ . This further supports the plasticization produced in the  
543 dispersed PLA phase, as described in detail in our previous studies.<sup>4,6,61</sup>

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/m<sup>2</sup>. 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-functionalizes vegetable oils and  
590 peroxides represents an attractive strategy to enhance the miscibility between green  
591 polyolefins and biopolyesters 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 use 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×,  
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.

735

Sample	Bio-HDPE (wt%)	PLA (wt%)	PE-g-MA (phr)	PE-co-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-g-MA	80	20	3	0	0	0
Bio-HDPE/20PLA+PE-co-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

736

737 **Table 2.** Mechanical properties in terms of tensile modulus ( $E_{\text{tensile}}$ ), maximum tensile  
 738 strength ( $\sigma_{\text{max}}$ ), elongation at break ( $\epsilon_b$ ), 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).

743

Sample	$E_{\text{tensile}}$ (MPa)	$\sigma_{\text{max}}$ (MPa)	$\epsilon_b$ (%)	Shore D hardness	Impact strength (kJ/m <sup>2</sup> )
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-g-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-co-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

744

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).

751

Sample	$T_{5\%}$ (°C)	$T_{deg1}$ (°C)	$T_{deg2}$ (°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-co-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

752

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).

758

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

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