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1 *Article*2 **Effect of compatibilizers on polyethylene-eucalyptus**  
3 **lignin blends**4 **Jérôme Vachon,<sup>1,\*</sup> Derar Assad-Alkhateb,<sup>1</sup> Laura de Araujo Hsia,<sup>2</sup> Jairo H. Lora,<sup>3</sup> Stéphanie**  
5 **Baumberger<sup>4</sup>**6 <sup>1</sup> SABIC Europe B.V., Urmonderbaan 22, 6160 AH Geleen, The Netherlands;7 <sup>2</sup> Suzano S/A; Estrada do Lageado, Lageado - Limeira, SP; CEP: 13486-199 Brazil8 <sup>3</sup> Lora Consulting LLC, 7 Camby Chase Rd, Media PA 19063, USA9 <sup>4</sup> Institut Jean-Pierre Bourgin, INRAE, AgroParisTech, Université Paris-Saclay, 78000 Versailles, France10 \*Correspondence to: J. Vachon (E-mail: [jerome.vachon@sabic.com](mailto:jerome.vachon@sabic.com))

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12 **Abstract:** Eucalyptus Kraft lignin was blended in various proportions with two different types  
13 of PE (LDPE and PCR), with or without compatibilizer (PE-GMA or PE-HEMA copolymers).  
14 Materials prepared by injection molding or extrusion casting were characterized for their thermal,  
15 antioxidant, antibacterial and mechanical properties. In addition, the photo-permeability was  
16 assessed, as this property is specifically relevant to mulching applications. The use of compatibilizers  
17 enhanced the antioxidant properties which reached more than 3 h OIT when lignin was present at 20  
18 wt% and beyond. Good antibacterial properties were obtained on Gram-positive bacteria when using  
19 PE-GMA as compatibilizer. The photo-permeability of the materials was also reduced, reaching a  
20 transmittance lower than 5% throughout the whole measurement range (200 - 800 nm) in PCR.  
21 However, higher lignin contents led to a more brittle material and the overall processability of the  
22 material became more difficult, features that were not improved by compatibilizers. These materials  
23 are promising candidates for mulching film application, especially with PCR which still lacks high-  
24 volume market applications.

25 **Keywords:** Lignin, LDPE, Post-Consumer Recycled plastics, Compatibilizer, Antioxidant,  
26 Antimicrobial, Mulching.  
2728 **1. Introduction**

29 In the last couple of decades, research efforts were concentrated on using ligno-cellulosic  
30 biomass as feedstock for the sustainable production of energy, chemicals and materials. Indeed, this  
31 ligno-cellulosic biomass can be recovered from forestry and agricultural residues as well as from  
32 dedicated energy crops, plants grown as a low-cost and low-maintenance harvest, which makes them  
33 a source of renewable carbon not competing directly with the supply of food resources for human  
34 and animal consumption.<sup>1</sup> Additionally, the ligno-cellulosic biomass has multi-million ton potential  
35 capacity, in particular its lignin component with a presence in biosphere estimated at ~ 350 billion  
36 tons.<sup>2</sup>

37 Lignin mass content determined by the Klason method reaches 25-35% in softwoods, 20-25% in  
38 hardwoods and 15-25% in herby plants.<sup>3</sup> It consists of a polymer built on phenylpropane-type  
39 monomers linked through various carbon-carbon and ether bonds making this raw material more  
40 resistant to chemical and enzymatic attacks than the other biomass components.<sup>4,5</sup> Several lignin  
41 isolation processes have been developed up-to commercial scale to valorize the carbohydrate  
42 fractions of wood and straws while producing a by-product so-called "technical lignin", recognized  
43 nowadays as high-value functional bio-based polymer with a wide range of applications.<sup>5,6,7</sup> Among  
44 these technologies, the Kraft process has the advantage to be versatile (applicable to both softwood  
45 and hardwood), to generate cellulosic fibers suitable for paper production, and to have the potential  
46 to produce large volumes of high purity lignin (less than 5% of carbohydrate contaminants). During  
47 the previous decade, worldwide Kraft lignin production capacity more than tripled reaching 120 kt

48 in 2016.<sup>8</sup> The main challenge for the industry and the scientific community remains the actual  
49 valorization of technical lignins and their use in high volume markets.<sup>9</sup> Promising markets are those  
50 of aromatics, carbon fibers, phenolic resins and additives for plastics, these last applications  
51 exploiting the multifunctionality of lignins.

52 In a previous paper, the use of specific lignin extracts as additives in high density polyethylene  
53 (HDPE) was reported.<sup>10</sup> It was observed that a fraction from annual plant soda lignin that possessed  
54 a high phenolic content (~ 4.2 mmol/g), conferred to the material specific attributes, when blended  
55 and co-extruded with HDPE at a few wt% level (ranges from 2 to 5). Besides antioxidant and  
56 antimicrobial properties (especially on Gram positive *Staphylococcus Aureus* bacteria), this lignin  
57 extract gave to the material repellent properties towards two types of insects, an invader (*Sitophilus*  
58 *oryzae*) and a penetrator (*Plodia interpunctella*). However, an issue when using lignins is the dark color  
59 and smell they confer to the material they are blended with, which constitutes a hurdle for potential  
60 application in food packaging (e.g as insect repellent films for protecting food). Another issue  
61 encountered is the poor compatibility of polyolefins with lignin, which can negatively affect the  
62 thermal and mechanical properties of polyolefins/lignin blends.<sup>11</sup> In the previous study, a poor  
63 compatibility between HDPE and the lignin fraction with low phenolic content ( $\leq 3.4$  mmol/g) was  
64 observed, leading to visible lignin agglomerates and film cracks even when lignin was used in low  
65 amounts (2 wt%). This phenomenon could be even more exacerbated when using higher lignin  
66 content and/or LDPE which is known to have a poorer compatibility with lignins than HDPE due to  
67 the interaction with branching, an entropically unfavorable feature.<sup>12</sup> To solve the compatibility  
68 problem, chemical modification of lignin is a potential route where the polarity of the lignin is  
69 modified,<sup>1a</sup> yet, the lignin functionality such as its antioxidant properties can be strongly altered. An  
70 advantageous alternative is the use of compatibilizers, materials that, through covalent bonding or  
71 polar interaction, act as a binder between materials of different polarities.<sup>11b,13</sup>

72 An interesting application for PE-lignin composites that could be targeted is for agricultural  
73 mulching films. Indeed, already colored material (with dyes or carbon black) are used and smell is  
74 not a limiting factor since the films are implemented in open space. Mulching is the practice of  
75 covering the soil surface with a thin plastic film around plants in their first growth stage for a rather  
76 short period, typically from 2 to 4 months but can be up to a couple of years depending on the quality  
77 of the material.<sup>14</sup> The films used for mulching are the second most important agricultural film  
78 applications after covers. The benefits achieved are soil moisture retention, heat trapping and  
79 controlling, improving cultivation conditions, enabling reduction of weeds and plant diseases,  
80 reducing the use of pesticides and preventing insects from attacking plants.<sup>15</sup> The most common  
81 material used for producing mulching films is LLDPE, sometimes used in combination with LDPE.  
82 Post-consumer recycled (PCR) materials that contain various sources of PE coming from mechanical  
83 recycling processes are increasingly used. Other materials such as EVA and EBA copolymers are also  
84 used for higher added value crops. Mulching films are commonly produced through an extrusion  
85 blown film process. The general procedure is to feed PE granules to a single screw extruder where  
86 material is melted and exits the die in the form of a tube. This tube is subsequently blown in a shape  
87 of a bubble which is collapsed and drawn upwards by two nip rolls. Finally, the obtained flattened  
88 tube is wound on a winder. The film thickness can range between ~15 to 80  $\mu\text{m}$  with a width up to 3  
89 m.<sup>16</sup> During the blown film process, the material is stretched in both the transverse and draw  
90 directions thus requiring that the material possesses a good mechanical strength which shall not  
91 altered by the addition of lignin. Additionally, puncture, impact strength resistance and ductility,<sup>17</sup>  
92 as well as a good UV and thermal stability are necessary during the lifetime of the film but also to  
93 sustain the blown film process which operates at high temperatures ( $\geq 190$  °C). To be attractive in a  
94 mulching application, the addition of lignin should not be detrimental to the original PE mechanical  
95 properties while conferring additional functionalities. For instance, photo-permeability is an  
96 important property for mulching films where blocking visible light transmission is key to prevent  
97 from an undesired high growth of weeds.<sup>18</sup> Carbon black, tannins and humic substances can be used  
98 to reduce the transmitted light.<sup>19</sup> Light transmittance also has an effect on soil temperature and

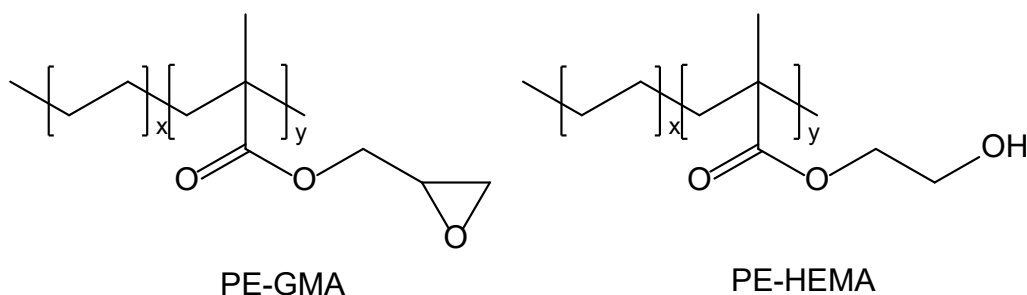
99 moisture retention. Furthermore, UV absorption may impact the kinetics of polymer degradation by  
 100 sun exposure, which could result in premature mechanical film failure.

101 The objective of this paper was to show that materials with enhanced properties (thermal  
 102 stability, mechanical strength, UV protection) can be prepared by blending LDPE with a lignin  
 103 fraction having a high phenolic content, in combination with compatibilizers. A eucalyptus Kraft  
 104 lignin was blended in various proportions with two different types of PE (LDPE and PCR), with or  
 105 without any compatibilizer (PE-copolymers). Materials prepared by injection molding or extrusion  
 106 casting were characterized for their thermal, antioxidant, antimicrobial, optical and mechanical  
 107 properties, as well as puncture resistance and photo-permeability, as these properties are specifically  
 108 relevant to mulching applications.

## 109 2. Materials and methods

### 110 2.1 Materials

111 SABIC® LDPE 2101N0W grade (MFR 0.85 dg/min at 190 °C and 2.16 kg) was used. The material  
 112 contains no additives. PCR-PE (RYMO W122 from Rymoplast) is a recycled PE that contains ~ 40%  
 113 LLDPE and ~60% LDPE, amounting overall to more than 99% recycled polymer content. NEWProd-  
 114 FP101 (provided by Suzano SA) is a high purity, low moisture renewable aromatic biopolymer  
 115 derived from eucalyptus wood pulped by the Kraft process and produced in a pilot plant using  
 116 proprietary technology (more technical specifications in Table 1). LOTADER® AX8840 or “PE-GMA”  
 117 (provided by Arkema) is a random copolymer of ethylene and glycidyl methacrylate (GMA),  
 118 polymerized by high-pressure autoclave process. The GMA content is ~8.0 wt% (determined by FT-  
 119 IR). PE-HEMA (provided by SABIC) is a copolymer based on a high-pressure free radical  
 120 copolymerization of ethylene and 2-hydroxyethyl methyl acrylate (HEMA) (Figure 1). The HEMA  
 121 content is ~17.6 wt% (determined by <sup>1</sup>H-NMR).  
 122



123

124 Figure 1. Chemical structures of PE-GMA and PE-HEMA. The ethylene and methacrylate blocks are randomly distributed

125 Table 1. Characteristics of NEWProd-FP101

<b>SOLID CONTENT</b>	wt%	>95
<b>LIGNIN</b>	wt%	>95
<b>HEMICELLULOSE</b>	wt%	<2
<b>ASH</b>	wt%	<3
<b>AROMATIC OH</b>	mmol/g	4.2
<b>T<sub>G</sub></b>	°C	~135
<b>APPARENT DENSITY</b>	kg/L	0.44 ± 0.04
<b>COMPACT DENSITY</b>		0.61 ± 0.07
<b>REAL DENSITY</b>		1.40 ± 0.02
<b>PH (10% AQ. SOLUTION)</b>		3 to 5

126

## 127 2.2 Polyethylene-lignin blends preparation

128 Polyethylene (LDPE and PCR), lignin and compatibilizers were ground by using cryogenic  
 129 conditions (with liquid nitrogen). The grinding and mixing process was performed by using an  
 130 Ultra Centrifugal Mill ZM 200. The lignin was dried in vacuum oven at 50 °C overnight prior to  
 131 compounding. PE and lignin mixtures were fed to a micro compounder machine (Xplore) with  
 132 two conical fully intermeshing mixing screws (capacity of 3 - 15 mL of material). The processing  
 133 temperature is controlled in 2 times 3 separate barrel-heating zones. The micro compounder was  
 134 fed with PE/lignin/compatibilizers ground mixtures through a powder feeder. All the samples  
 135 were processed at a maximum rotor speed of 170 RPM for 5 min at 150 °C. The following  
 136 materials were made with LDPE and PCR-PE base polymers at varying concentration of each  
 137 constituent (Table 2).

138 Table 2. List of compounded materials

Sample name	Composition
LDPE-1	LDPE (95 wt%) + FP101 (5 wt%)
LDPE-2	LDPE (94 wt%) + FP101 (5 wt%) + PE-GMA (1 wt%)
LDPE-3	LDPE (94 wt%) + FP101 (5 wt%) + PE-HEMA (1 wt%)
LDPE-4	LDPE (88 wt%) + FP101 (10 wt%) + PE-GMA (2 wt%)
LDPE-5	LDPE (76 wt%) + FP101 (20 wt%) + PE-GMA (4 wt%)
LDPE-6	LDPE (64 wt%) + FP101 (30 wt%) + PE-GMA (6 wt%)
PCR-PE1	PCR-PE (95 wt%) + FP101 (5 wt%)
PCR-PE2	PCR-PE (94 wt%) + FP101 (5 wt%) + PE-GMA (1 wt%)
PCR-PE3	PCR-PE (94 wt%) + FP101 (5 wt%) + PE-HEMA (1 wt%)
PCR-PE4	PCR-PE (76 wt%) + FP101 (20 wt%) + PE-HEMA (4 wt%)

139 Xplore micro-injection molder was used to obtain materials in desired shapes (plaques and bars).  
 140 The molder consists of a temperature-controlled mold, connected with a heated removable injection  
 141 nozzle unit. PE/lignin/compatibilizers were injected into the temperature-controlled mold with a  
 142 plunger powered by compressed air (pressure ~10 bars, mold temperature 40 to 60 °C).  
 143

144 Films from PE/lignins/compatibilizers blends were produced by extrusion casting process  
 145 (thickness ~ 60 to 70 µm in the middle and 100 to - 120 µm at the edge of the films, width = 70  
 146 mm). The prepared pellets were let to dry at 70 °C for 2 h. All films were prepared by using the  
 147 following parameters: extrusion temperature = 150 °C, temperature at the shaping die = 174 °C,  
 148 extruder speed = 135 RPM and films thickness = 60-100 µm.

## 149 2.3 Material characterization

150 Thermogravimetric Analyses (TGA) were performed by using a TA instruments equipment. All  
 151 measurements were performed under nitrogen from 30 to 300 °C with 10 °C/min heating rate.  
 152 Isothermal TGA was performed at 200 °C.

153 Differential scanning calorimetry (DSC) measurements were performed on a TA Instruments  
 154 Q20 equipped with a RCS 90 cooling system. About 3 – 5 mg of polymeric sample was weighed inside  
 155 an aluminum pan and subjected to DSC measurements under nitrogen atmosphere. Unless otherwise  
 156 noted, polymers were scanned twice from -100 °C to 200 °C at a constant heating/cooling rate of 20  
 157 K/min. The  $T_m$ , and the melting enthalpy ( $H_m$ ) were determined from the second heating.

158 Oxidation Induction Time (OIT) was measured by DSC on molten polymer according to  
 159 standard ASTM D3895. About 3 – 5 mg of polymeric sample was weighed inside an aluminum pan  
 160 and subjected to DSC measurements under nitrogen atmosphere (50 mL/min). The polymer was  
 161 heated until 200 °C at 10 °C/min heating rate and left at this temperature for 5 min. Nitrogen was  
 162 switched to oxygen and the time before an exothermal peak is detected was recorded.

163



#### 164 2.4 Optical properties

165 Haze measurements of the cast films were performed according to the “Standard Test Method  
166 for Haze and Luminous Transmittance of Transparent Plastics” ASTM D1003-C using a BYK Gard-i  
167 device where the opening angle of the beam passing through the sample is less than 3°. The roll was  
168 clamped on the holder in front of the detector. The average of 5 measurements is reported where  
169 random spots on the films were chosen at different height and length of the film. For the gloss, BYK-  
170 micro-gloss 45° (typical angle used for films) was used where a black felt was placed below the film  
171 as background to diffuse the light during measurement. The average of 5 measurements is reported  
172 where random spots on the films were chosen at the same height. Due to the width of the device  
173 which is close to the one of the film, and to be sure that the device fully covers the film, the device  
174 was placed in the middle of the film thus only measuring the middle part and not at the edges.

175 Photo-permeability (UV-Vis) measurement were performed to determine the percentage of light  
176 transmittance at different wavelengths between (200 and 850 nm) by using an ultraviolet-visible (UV-  
177 Vis) spectrophotometer. The transmission (in %) is shown with sample thickness correction to  
178 account for variations.

179

#### 180 2.5 Mechanical properties

181 Mechanical properties (tensile strength, Young’s modulus, maximum elongation at break) were  
182 measured by using ISO 527 (Plastics – Determination of tensile properties) and Zwick-Roell machine  
183 for both tensile bars and cast films. Tests were performed on five specimens for both tensile bars and  
184 cast films. The films were cut with the following dimension: thickness = 60-110 µm, width = 15 mm,  
185 length = 50-53 mm. Measurements were performed on both TD direction and MD direction at room  
186 temperature (test speed = 50 mm/min). Sample thickness was taken into account in the calculation to  
187 get rid of variations due to this parameter. The same tensile bars were used to measure Izod  
188 Pendulum Impact Resistance. Tests were performed on three specimens at -30 °C, both on notched  
189 and un-notched samples according to ASTM D256 (“Standard Test Methods for Determining the Izod  
190 Pendulum Impact Resistance of Plastics”).

191 Puncture resistance of the films were measured according to the “Slow Rate Penetration  
192 Resistance of Flexible Barrier Films and Laminates” test ASTM F1306. Experiments were performed  
193 at 23 °C using a clamping fixture diameter of 34.9 mm, a pre-load of 0.2 N and a test speed of 25  
194 mm/min. Specimens with approximate dimensions of 60x60 mm were cut from the films and  
195 clamped. The penetration hole was ~35 mm in diameter and a hemispherical penetration probe of 3.2  
196 mm diameter was used. Reported results are the average measurement of 5 specimens.

#### 197 2.6 Antibacterial properties

198 Antimicrobial activity measurements were performed following ISO 22196 “Measurement of  
199 antibacterial activity on plastics and other non-porous surfaces” and was performed at Industrial  
200 Microbiological Services LTD using the following conditions. The films were cut into ~50 ×50 mm  
201 squares. An aliquot (225 µL) of a log phase cell suspension of either *Escherichia coli* ( $4.2 \times 10^5$   
202 cells/mL; ATCC 8739) or *Staphylococcus aureus* ( $4.1 \times 10^5$  cells/mL; ATCC 6538p) prepared using the  
203 method described in ISO 22196:2011 was held in intimate contact with each of the three replicates of  
204 films supplied using a 30 × 30 mm PE film (cut from a sterile Stomacher bag). The temperature of  
205 incubation was set to  $35 \pm 2$  °C. The size of the surviving population was determined using the  
206 method described in ISO 22196 : 2011. The viable cells in the suspension were enumerated by spiral  
207 dilution on to Trypcase Soya Agar and by the pour plate method described in ISO 22196. These plates  
208 were then incubated at  $35 \pm 2$  °C for 24 h and then the colonies present are counted. An additional  
209 three replicates of unfortified surfaces (LDPE films) were also inoculated in the manner described  
210 above but were then analysed immediately for the size of microbial population present to provide 0-  
211 time control data). Antimicrobial activities are given in logarithmic reduction R. R is calculated  
212 according to the bacterial concentration in the negative control and the concentration after 24 h of  
213 contact with the treated products. All data were converted to colony forming units (CFU) cm<sup>-2</sup> and

214 then transformed (Log10) to provide a data set that conformed to a Gaussian distribution. Potential  
215 outliers were tested using Dixon's Q-test ( $P = 0.05$ ). Statistical significance of any effects in the dataset  
216 was tested by analysis of variance (ANOVA,  $P = 0.05$ ) and the confidence intervals of the means were  
217 calculated and displayed as Box and Whisker plots (see Sup. Info. for further details).

### 218 3. Results and Discussion

219 In order to investigate the benefit of compatibilizers on the properties of PE-lignin blends, a  
220 pilot-plant pre-commercial eucalyptus Kraft lignin sample (NewProd-FP101, Suzano SA) was used.  
221 This sample was selected for its (i) high lignin content, (ii) low content of moisture, sugars and ash,  
222 (iii) low molecular weight, and (iv) low softening temperature compared to other commercially  
223 available Kraft lignins and lignosulfonates (Table 1), which made it a good candidate for the  
224 preparation of homogeneous blends. Lignin incorporation rate up to 30% was tested, since it is the  
225 limit mentioned in literature at which most of polymer-lignin blends lose their mechanical  
226 properties.<sup>20</sup> The two compatibilizers tested (PE-GMA and PE-HEMA) were incorporated at 1:5 wt.  
227 ratio with respect to lignin. The compatibilizers were selected due to their difference in polarity and  
228 reactivity.<sup>21</sup> While the HEMA group can participate in both hydrogen donor and acceptor, GMA can  
229 only participate as hydrogen acceptor. Additionally, the epoxide from the glycidyl group can  
230 undergo an opening reaction with nucleophilic groups such as hydroxyl and, carboxyl groups which  
231 are present in lignins.<sup>22</sup> This section reports on the properties of the different materials obtained.

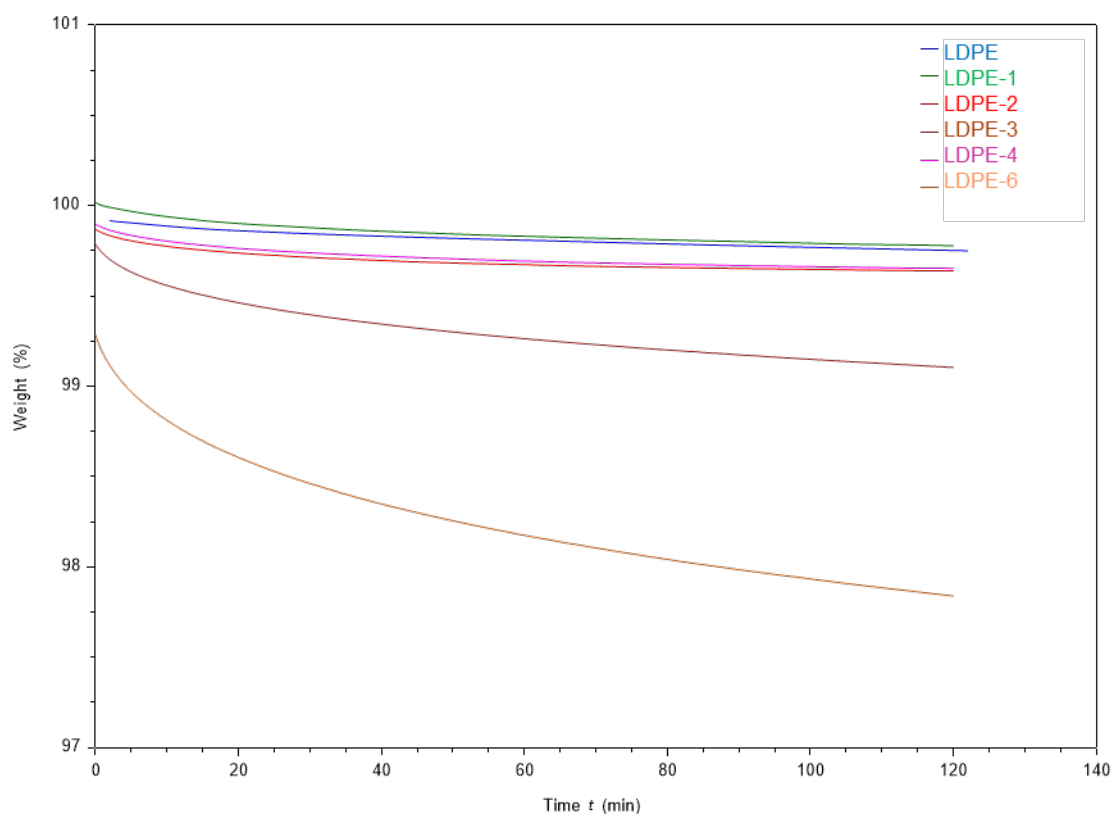
#### 232 3.1. Thermal stability

233 The thermal stability of the films made out of lignin is key for assessing the processability of  
234 such materials. Technical lignins are known to have limited thermal stability which is indicated by  
235 TGA by some weight loss when temperature exceeds 190 °C as has been reported previously,<sup>10</sup> and  
236 confirmed for the lignin sample used in this study (Figure S1). An isothermal TGA at 200 °C for 2 h  
237 was thus performed on the PE-lignin blends to evaluate their relative thermal stability under  
238 temperature and time more severe than those used in normal processing, for instance in extrusion or  
239 film blowing (Figure 2). Under these conditions, the lignin FP101 experienced an 8.2% weight loss  
240 while both reference PE materials (LDPE and PCR-PE) only showed 0.2% weight loss (Table 3). When  
241 ramping up the temperature to 200 °C, before starting the isothermal TGA experiment, the lignin  
242 already lost ~4 wt%, while the LDPE and PCR-PE materials were mostly unaffected (Figure S2 and  
243 S3). Lignin being somewhat moisture sensitive, this could be related to water loss as this weight loss  
244 happened around 100 °C. To tentatively minimize this effect in compounded materials, the lignin  
245 was dried prior to compounding. However, the molten polymer exiting the extruder was cooled in a  
246 water bath before pelletizing so that there was no control on the extent of moisture present in the  
247 lignin within the polymer. The weight loss during the temperature ramp-up of PE-lignin blends was  
248 negligible ( $< 0.5$  wt%) at low lignin content (5 wt%), but starts to be significant, as shown for PCR-  
249 PE4, at 20 wt% lignin content. There, 1 wt% was already lost before starting the isothermal  
250 experiment. Results showed only minimal weight loss of the LDPE samples containing 5 wt% lignin  
251 after 2 h, which reflected a good thermal stability of the materials. In LDPE-6 (containing 30 wt% of  
252 lignin), an increased weight loss was observed (1.4 wt%), reflecting the presence of 6 times the  
253 amount of lignin in LDPE-1 material. PCR-PE materials containing 5 wt% lignin showed a slightly  
254 higher weight loss compared to LDPE based blends of similar lignin content, yet differences remain  
255 low and in the order of magnitude expected regarding the content of lignin. Regarding PCR-PE4, a  
256 lower weight loss was recorded with respect to the lignin content (9 wt% vs e.g 14 % for PCR-PE1  
257 containing 5 wt% of lignin), however, considering the additional 1 wt% weight loss during the  
258 temperature ramp-up, the true weight loss would be in the same range (2.8 wt% would correspond  
259 to ~ 14 wt% based on the lignin content). Overall, besides some moisture related weight loss, the PE-  
260 lignin blends experienced only slight weight loss that would not be detrimental when subjecting  
261 them to a blow molding process.

262 Table 3. Weight loss of lignin, PE and PE-lignin blends measured by TGA

Sample	Weight loss (%) at 200 °C after 120 min	Weight loss (%) / wt% of lignin in PE at 200 °C after 120 min
FP101	8.2	-
LDPE-ref	0.2	-
LDPE-1	0.2	4
LDPE-2	0.3	6
LDPE-3	0.3	6
LDPE-4	0.7	7
LDPE-6	1.4	5
PCR-PE-ref	0.2	-
PCR-PE 1	0.7	14
PCR-PE 2	0.6	12
PCR-PE 3	0.8	16
PCR-PE 4	1.8	9

263



264

265 Figure 2. TGA curves of LDPE materials in isothermal experiments at 200 °C

## 266 3.2. Influence on crystallinity

267 DSC measurements were first performed to evaluate the impact of lignin onto PE's initial  
 268 crystallinity ( $X_c = 50\%$ ) (Table 4, Figure S2). Increasing lignin content into PE led to a decrease of the  
 269 material's crystallinity. However, taking into account the amorphous characteristic of lignin (Figure  
 270 S3), a higher decrease would be expected based on the dilution factor due to lignin incorporation in  
 271 the crystalline PE matrix. For instance, at 30 wt% lignin incorporation rate, a total material  
 272 crystallinity of 35 % still remained (entry 7). This cannot be attributed to lignin particles acting as a  
 273 nucleating agent for PE, as a true indication of nucleating ability for a nucleating agent is the increase  
 274 of the crystallization point. In this case, there is basically no change. Instead, it is suspected that water



275 which might be absorbed by lignin influences the melting enthalpy value measured. Enthalpy of  
 276 vaporization of water is 2260 J/g, which is one order of magnitude higher than melting enthalpy of  
 277 PE, and occurs within the melting range of PE. The incorporation of a compatibilizer in a PE-lignin  
 278 system did not change the apparent PE crystallinity as for instance a similar crystallinity was  
 279 observed between LDPE-1 and LDPE-2. DSC measurements were also performed on PCR materials  
 280 and details are shown in supporting information (Table S2 and Figure S4 to S8). A similar statement  
 281 as for LDPE can be made, as the addition of up to 20% did not significantly affect neither melting and  
 282 crystallization temperatures, nor the degree of crystallinity compared to the PCR-PE reference.  
 283 However, due to the presence of two different types of PE in PCR-PE, two peaks were observed for  
 284 both melting and crystallization, with a relatively broad DSC curve which made the variations  
 285 induced by the presence of lignin in the material insignificant.

286  
 287 *Table 4. Thermal data and crystallinity of LDPE-lignin blends measured by DSC*

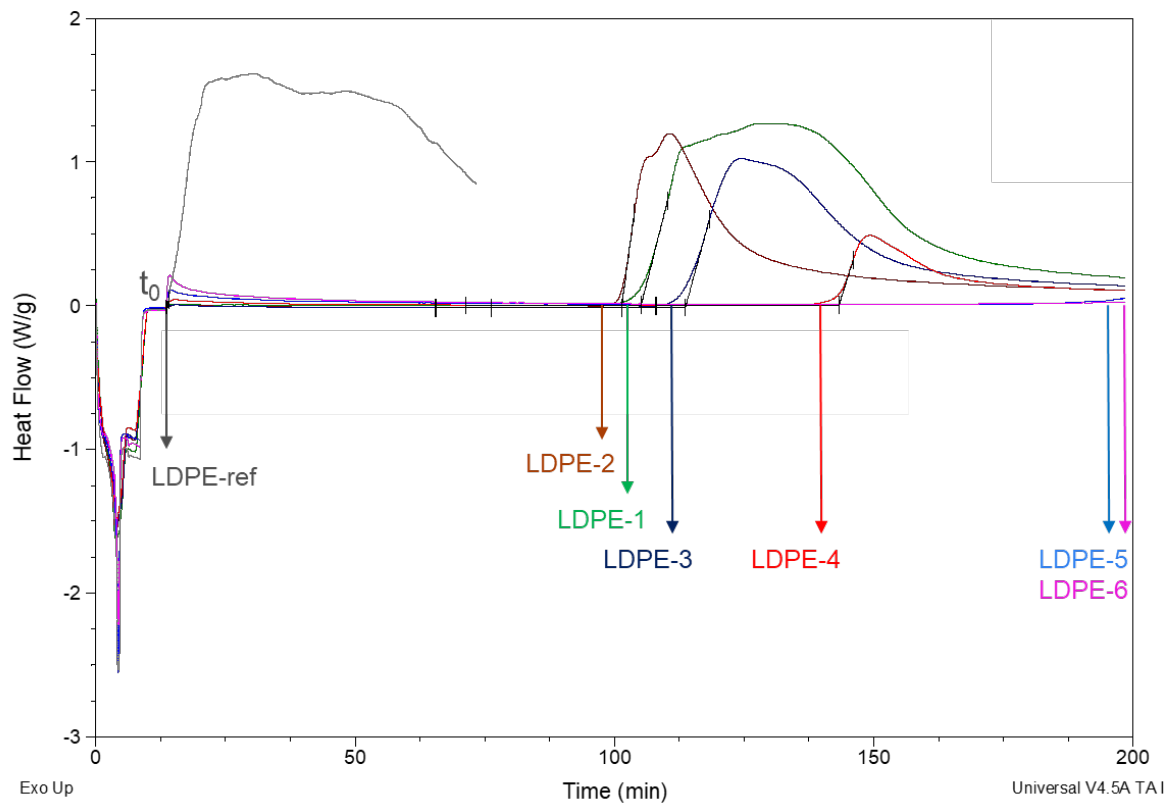
Entry	Sample	T <sub>c</sub> (°C) <sup>a</sup>	ΔH <sub>c</sub> (J/g) <sup>a</sup>	T <sub>m</sub> (°C) <sup>a</sup>	ΔH <sub>m</sub> (J/g) <sup>a</sup>	Total X <sub>c</sub> (%) <sup>b</sup>
1	LDPE-ref	99.5	192.9	100.2	143.6	50
2	LDPE-1	99.0	195.5	100.0	140.8	49
3	LDPE-2	98.9	192.0	101.0	138.5	48
4	LDPE-3	99.0	180.6	101.2	124.2	43
5	LDPE-4	98.7	176.2	100.0	130.7	46
6	LDPE-5	98.8	167.3	101.0	116.8	41
7	LDPE-6	98.6	149.8	100.0	101.0	35
8	PCR-PE-ref	110.2	130.2	112.3	131.0	46
9	PCR-PE-1	109.9	141.5	114.7	131.8	46
10	PCR-PE-2	110.0	167.2	114.8	142.8	50
11	PCR-PE-3	110.0	148.9	115.2	127.3	45
12	PCR-PE-4	109.4	129.1	108.9	117.8	41

288 a. Det. via DSC. For PCR-PE materials, onset T<sub>c</sub> and T<sub>m</sub> are reported. See supporting info for the full details; b. Degrees of crystallinity (X<sub>c</sub>)  
 289 were calculated dividing the melting enthalpy of 100 % crystalline PE (286.2 J·g<sup>-1</sup>) according to ref.<sup>23</sup> The melting enthalpy was determined  
 290 from the DSC second heating scan.

### 291 3.3 Antioxidant properties

292 The antioxidant properties conferred to PE by lignins with high phenolic content were recently  
 293 reported,<sup>10</sup> and this antioxidant effect of lignins has been established for a broad range of lignin-  
 294 polyolefins blends.<sup>24</sup> In this study, the effect of compatibilizers on the antioxidant properties of the  
 295 LDPE-lignin blends was determined using OIT measured by DSC on molten polymer (Figure 3). OIT  
 296 has been shown to be a robust analytical method for determining antioxidant performances in  
 297 polyolefins, where the concentration of phenolic antioxidants (above 100 ppm level) was found  
 298 linearly correlated with measured induction times.<sup>25</sup> In agreement with the fact that LDPE was  
 299 unstabilized, an immediate thermal oxidation occurred within a few seconds (entry 1). With 5 wt%  
 300 of lignin, an antioxidant effect was observed with 91 min OIT (entry 2), which was of the same order  
 301 but yet exceeded the 80 min OIT previously reported for the extract from annual plant soda lignin.<sup>10</sup>  
 302 While the addition of 1 wt% PE-GMA did not increase OIT, PE-HEMA further enhanced the lignin  
 303 antioxidant properties with an OIT of 100 min. Since compatibilizers do not possess any antioxidant  
 304 properties by themselves, the increased OIT could be explained by a better dispersion of the lignin  
 305 within the PE material, or by indirect contribution to radical stabilization through matrix effect. OIT  
 306 was further increased when using higher lignin content, achieving for instance an over 3 h protection  
 307 (no measure was performed for longer times) for lignin incorporation rate equal to or higher than 20  
 308 wt%. This result confirmed that lignin possessing high phenolic content can provide outstanding  
 309 antioxidant properties and that, at high loading content with the use of a compatibilizer, a long life-  
 310 time protection could be achieved. As a matter of comparison, tetrakis-(methylene-3-(3,5-di-tertbutyl-  
 311 4-hydroxyphenyl)-propionate methane ("Irganox 1010"), a phenolic antioxidant traditionally used in

312 polyolefins, led to an OIT of ~60 min at 0.25 wt% loading in HDPE (which is on the high range in  
 313 commercial polyolefins).<sup>25</sup> OIT being proportional to antioxidant concentrations, it means that at least  
 314 0.75 wt% of Irganox 1010 would be necessary to reach more than 3 h of OIT. Interestingly, the  
 315 structure of the compatibilizer influenced the lignin properties in the matrix. The more beneficial  
 316 effect of PE-HEMA compared to PE-GMA may be explained by different factors. First, the amount of  
 317 HEMA was higher than the amount of GMA in the PE-copolymers. Secondly, HEMA did not alter  
 318 the functionalities of the lignin as interacting only through H-bond while GMA could potentially  
 319 react with the OH and CO<sub>2</sub>H groups of the lignin.  
 320



321  
 322 Figure 3. OIT Measurements of LDPE and LDPE-lignin blends

323

Table 5. OIT of LDPE and LDPE-lignin blends

Sample	OIT (min)
LDPE-ref.	<0.5
LDPE-1	91
LDPE-2	87
LDPE-3	100
LDPE-4	129
LDPE-5	> 180
LDPE-6	> 180

324

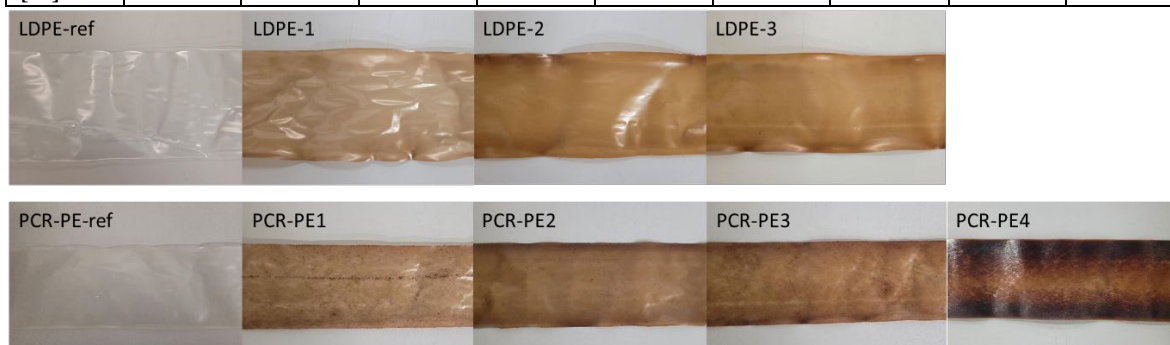
## 325 3.4 Optical properties

326 Haze and gloss measurements were performed to assess the effect of lignin on the films  
 327 aspect and to infer any effect of compatibilizers (Table 6, Figure S11 and S12). The images of the  
 328 film (Figure 4) indicated that more black particles were present in uncompatibilized films (LDPE-  
 329 1 and PCR-PE1), with a more pronounced effect in the PCR-PE material. It could be deduced  
 330 from the visual appearance of the films that PE-GMA was a more effective compatibilizer of the  
 331 system than PE-HEMA, as the films appeared more homogeneous and with lower proportion  
 332 of black particles, especially by comparison of LDPE-2 and LDPE-3. This was confirmed by a  
 333 lower haze and higher gloss performance of such materials. However, haze and gloss are  
 334 dominated by surface roughness. For instance, a higher gloss in LDPE-2 means that a less rough  
 335 surface was obtained when compared to uncompatibilized LDPE-1. For PCR-PE4 containing 20  
 336 wt% of lignin, a high haze was obtained, which matches the visual appearance of the film, but  
 337 also a higher gloss was noticed compared to all the other PCR-PE films. However, due to the  
 338 size of the gloss-meter, only the middle part of the film could be measured which appears  
 339 drastically different than the edges. Overall, the cast films produced show a different thickness  
 340 at the edges (60 to 70  $\mu\text{m}$ ) compared to the center of films (100 to 120  $\mu\text{m}$ ). The addition of lignin  
 341 leads to a bigger discrepancy between the thickness of the edges (which appear slightly darker)  
 342 and the one in the center. It is the most pronounced in PCR-PE4 where up to 200  $\mu\text{m}$  thickness  
 343 was measured at the edges while only  $\sim 100$   $\mu\text{m}$  was measured in the center. Hence, the apparent  
 344 film inhomogeneity only allows to draw conclusions on optical properties in the center of the  
 345 film, which is not representative of the whole film.

346

347 *Table 6. Haze and gloss measurements of the cast films*

	LDPE- ref	LDPE- 1	LDPE- 2	LDPE- 3	PCR- PE-ref	PCR- PE-1	PCR- PE-2	PCR- PE-3	PCR- PE-4
Haze [%]	28.6 $\pm$ 0.5	59.0 $\pm$ 0.3	50.0 $\pm$ 0.9	73.1 $\pm$ 0.9	50.0 $\pm$ 0.3	75.4 $\pm$ 0.6	80.0 $\pm$ 0.5	80.2 $\pm$ 0.5	87.6 $\pm$ 0.7
Gloss [%]	4.3 $\pm$ 1.1	13.5 $\pm$ 3.1	16.5 $\pm$ 3.1	11.7 $\pm$ 2.8	7.8 $\pm$ 2.7	6.5 $\pm$ 1.2	6.0 $\pm$ 0.7	7.4 $\pm$ 1.4	14.2 $\pm$ 0.5



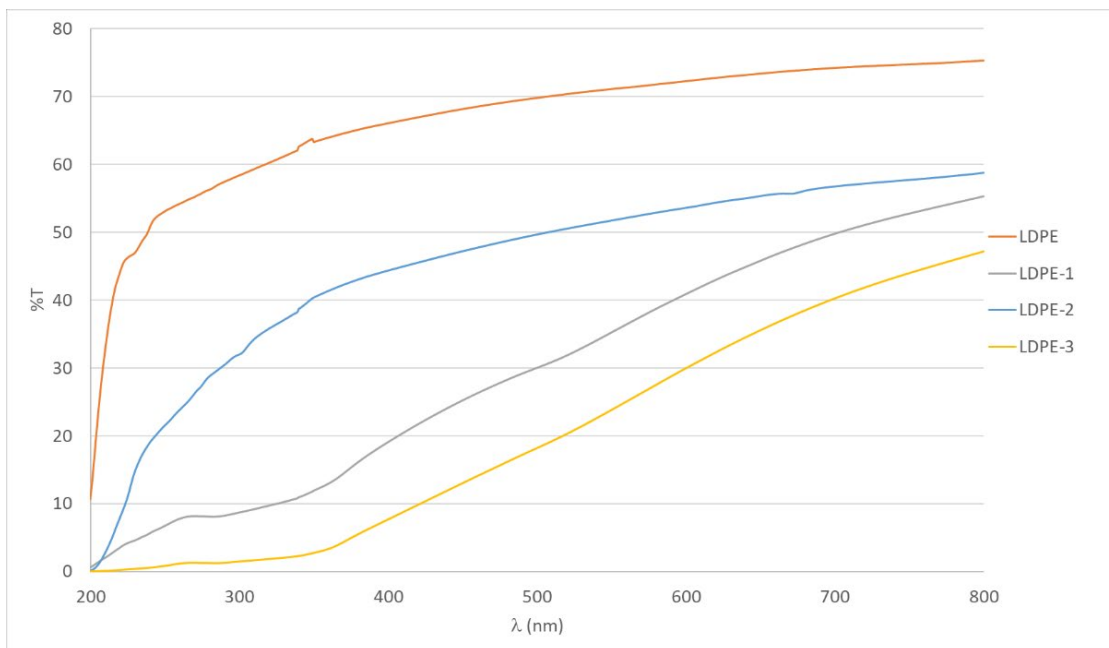
348

349 *Figure 4. Images of cast films*

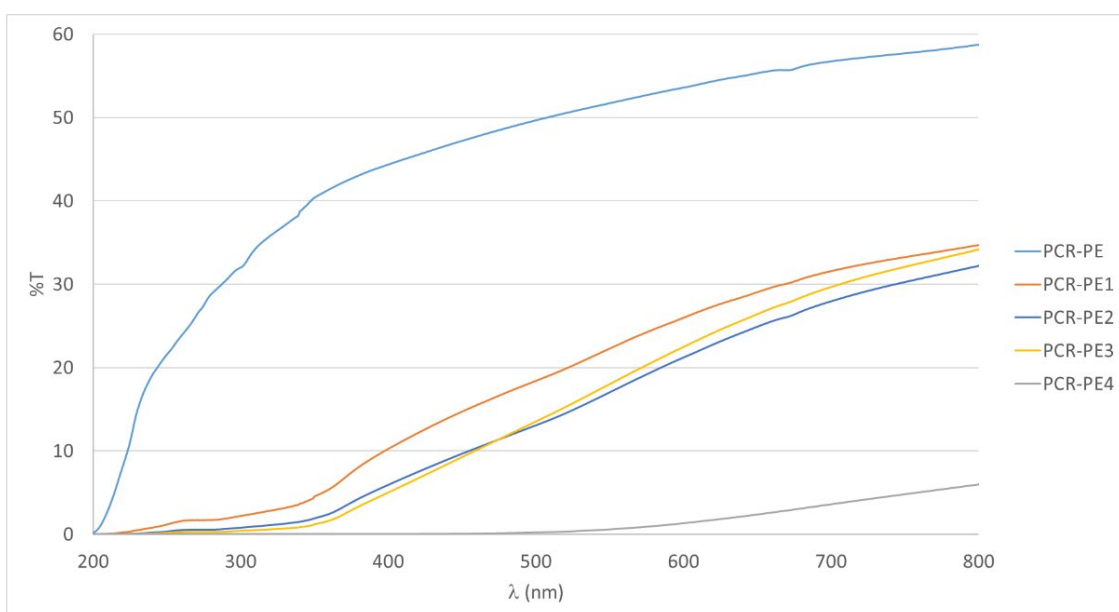
## 350 3.5 Photo-permeability (UV-Vis) results

351 Photo-permeability of the lignin-PE blends was measured (Figure 5) on films (Figure S18)  
 352 relative to the transmittance of virgin LDPE and PCR. The transmittance of LDPE increased  
 353 significantly at higher wavelengths going from  $\sim 50\%$  at 250 nm to  $\sim 75\%$  at 800 nm. The addition  
 354 of 5 wt% of lignin (in the absence of any compatibilizer) not only retarded this phenomenon, but  
 355 also lowered drastically the transmittance throughout the whole measurement range. For  
 356 instance, the transmittance %T remained below 10% up to 380 nm to only climb up to 55% at 800  
 357 nm. While the extra addition of PE-GMA compatibilizer slightly increased the photo-  
 358 permeability of the film, PE-HEMA on the contrary resulted in an additional 10% decrease of

359 transmittance throughout the whole measurement range. Thus, an almost complete absorption  
 360 was still observed up to 400 nm. Such result is similar to the performance of TiO<sub>2</sub> at 2 wt%  
 361 loading which gives 0% transmission in the region of 200-350 nm.<sup>26</sup> The PCR-PE material (Figure  
 362 6), already absorbed more UV than virgin LDPE and had only 60% transmittance at 800 nm.  
 363 Again, the addition of 5 wt% lignin decreased drastically UV transmittance which remained  
 364 pretty flat up to 400 nm. The presence of compatibilizers (PE-GMA and PE-HEMA) did not affect  
 365 spectrophotometric properties. Only through the increase of lignin content, an almost full UV  
 366 absorption was observed with a transmittance lower than 5% throughout the whole  
 367 measurement range when 20 wt% of lignin was used. Such a material would thus fulfill the  
 368 requirements of mulching films in terms of photo-permeability while having outstanding  
 369 antioxidant properties.



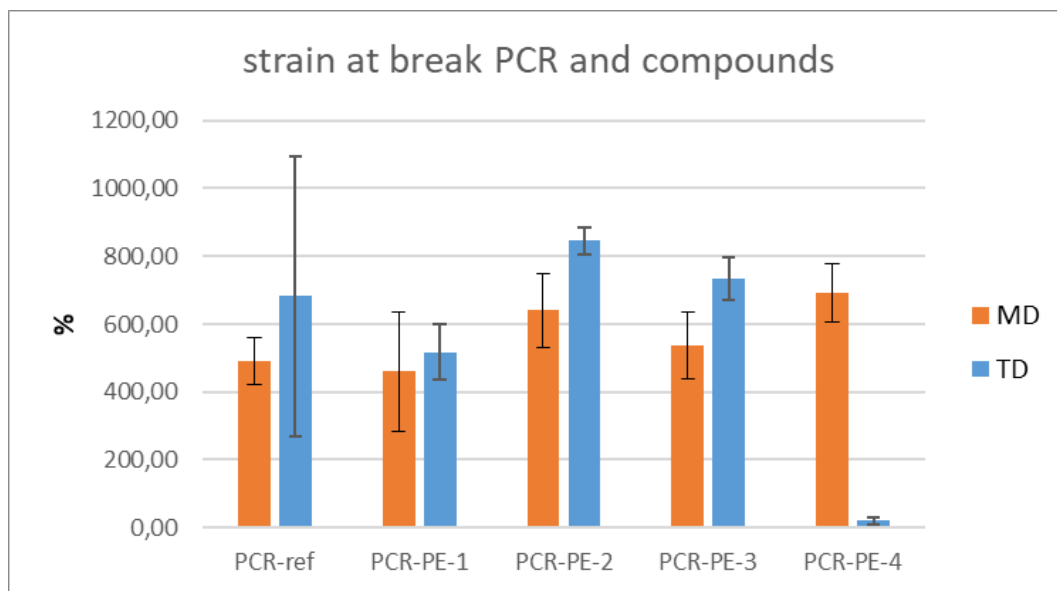
370

371 *Figure 5. % transmittance of LDPE and LDPE-lignin blends films*

372

373 *Figure 6. % transmittance of PCR and PCR-lignin blends films*374 **3.5 Mechanical properties**

375 The effect of lignin on LDPE and PCR was assessed by measuring the yield stress, strain at  
 376 break as well as the modulus on both injection molded bars and films (on machine direction MD  
 377 and transverse direction TD, Figure S13 to Figure S24). Regarding LDPE films, the addition of 5  
 378 wt% lignin alone did not alter much the original material mechanical properties, enhancing them  
 379 in some instances. Interestingly, the addition of PE-HEMA provided a little improvement.  
 380 However, it appeared difficult to make films of good quality with the samples containing higher  
 381 amounts of lignin. Regarding PCR films, the addition of 5 wt% lignin alone negatively affected  
 382 the mechanical properties of the material. The addition of 1 wt% of PE-GMA restored values  
 383 close to original levels. This result was consistent with the visual observation where PCR-PE  
 384 films containing PE-GMA were of superior quality compared to uncompatibilized PCR-PE and,  
 385 to a lower extent, to the one containing PE-HEMA. Furthermore, PCR-PE2 film, which showed  
 386 the best visual aspect, had the highest strain at break on both machine and transverse directions,  
 387 due to the absence of stress concentrators in the films with better homogeneity (Figure 7). When  
 388 using 20 wt% lignin content and PE-HEMA as compatibilizer, materials became harder and less  
 389 deformable which was particularly noticed in TD as films broke at very low strain. With  
 390 increased hardness (modulus) the materials also become more sensitive to stress concentration  
 391 as the stress intensity increases with increasing modulus.



392

393 *Figure 7. Tensile test on PCR films: strain at break*

394 For studying materials with higher amount of lignin, injection molding of thick objects was  
 395 necessary. A similar observation was made compared to the films, for both PCR and LDPE  
 396 materials. The addition of lignin did make the material harder but more brittle as shown by the  
 397 decreased strain at break. It was particularly noticeable with the highest amounts of lignin used.  
 398 The compatibilizer did not induce major changes compared to the control (LDPE-1 vs LDPE-2).  
 399 This behavior was further confirmed by the Izod impact test on notched specimen at -30 °C  
 400 (Figure S30). Since mulching films experience a wide range of temperatures, the test was  
 401 performed at low temperature to help gauge the impact resistance of the material in cold  
 402 environments. Starting from a 75% ductile LDPE material, lignin addition led to a complete loss  
 403 of ductility which was not mitigated by the compatibilizer (Table 7).

404

405

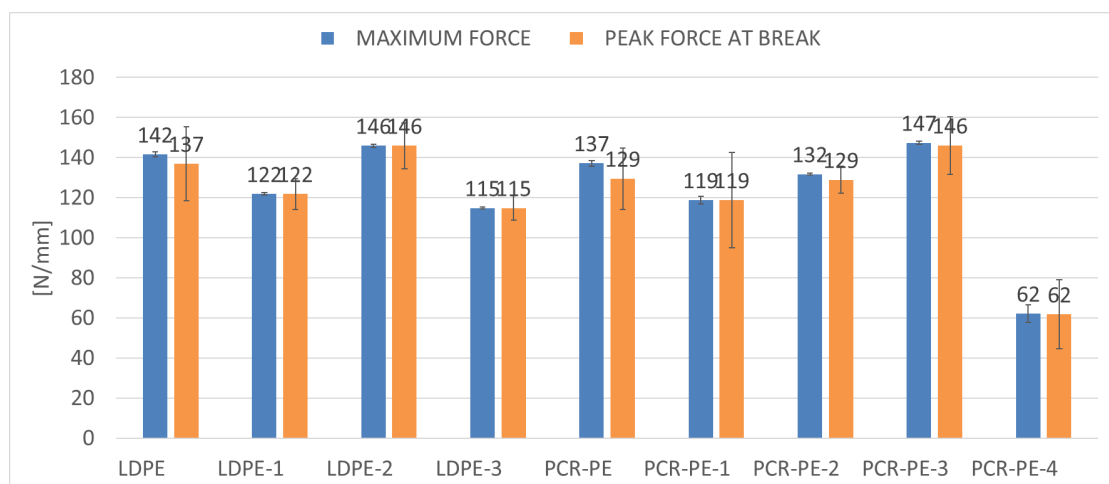
406

407 Table 7. Izod impact results on IM LDPE, Notched -30 °C

		LDPE	LDPE-1	LDPE-2	LDPE-4	LDPE-6
<b>Ductility</b>	<b>%</b>	<b>75</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>
<b>Impact Strength-Avg</b>	<b>J/m</b>	<b>660</b>	<b>52,3</b>	<b>48.0</b>	<b>46.0</b>	<b>32,2</b>
<b>Impact Strength-Std</b>	<b>-</b>	<b>392</b>	<b>5,0</b>	<b>5,6</b>	<b>8,2</b>	<b>6,7</b>
<b>Impact Strength-Rsd</b>	<b>%</b>	<b>59,5</b>	<b>9,5</b>	<b>11,6</b>	<b>17,9</b>	<b>20,8</b>

## 408 3.6 Puncture resistance

409 The maximum force, the peak at force (Figure 8) and the energy at break (Figure S25) were  
 410 calculated from the puncture resistance test. Due to thickness differences between the films,  
 411 results were corrected for thickness variations. In all cases, the addition of 5 wt% lignin  
 412 decreased the puncture resistance, as can be seen for LDPE-1 and PCR-PE1. PE-GMA boosted  
 413 the performance of the LDPE blend, slightly surpassing the LDPE values while PE-HEMA did  
 414 not provide any improvement. For PCR-PE, PE-GMA restored the performance back to the  
 415 original values, but interestingly, in this case PE-HEMA was a slightly more effective  
 416 compatibilizer. Again, at high loading content such as in PCR-PE4, the material showed a brittle  
 417 elastic fracture at a relatively low force which was not mitigated by the presence of the  
 418 compatibilizer.

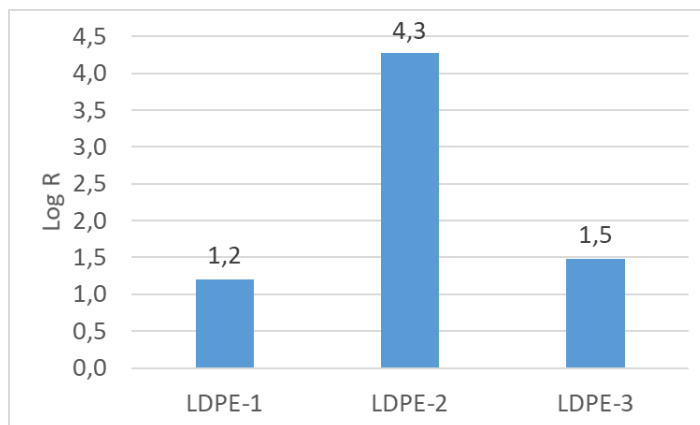
419  
420 Figure 8. Puncture resistance measurement

## 421 3.7 Antibacterial properties

422 Some LDPE-lignin films were subjected to the antibacterial test according to ISO22196  
 423 standard, using an LDPE film without any additive as control. To study the influence of the  
 424 compatibilizer, we selected LDPE-1 (containing 5 wt% lignin), LDPE-2 (using additionally 1wt%  
 425 PE-GMA) and LDPE-3 (using additionally 1wt% PE-HEMA), results are shown in Figure 9 (see  
 426 Figure S26, Table S3 to S8 for additional details and analyses of variance). All LDPE films did  
 427 not display any antibacterial activity towards *E. coli*. LDPE-1 showed a small bacterial reduction  
 428 on *S. aureus* (log R = 1.2, i.e 94% reduction) which was only slightly enhanced in presence of PE-  
 429 HEMA compatibilizer (LDPE-3: log R = 1.5, i.e 97% bacterial reduction). Interestingly the  
 430 presence of PE-GMA compatibilizer in LDPE-2 provided a full bacterial reduction (log R > 4.3,  
 431 i.e bacterial reduction >99.99%). A similar observation was made in our previous study on HDPE  
 432 where films containing 5 wt% of a lignin extract with high phenolic content displayed  
 433 antibacterial properties only towards the gram-positive bacteria *S. aureus*.<sup>10</sup> This result was  
 434 consistent with the fact that gram-positive bacteria are more sensitive towards antibacterial



435 substances than gram-negative bacteria because of their cell wall structure which is protected by  
 436 an outer membrane.<sup>27</sup> These current results further showed that the antibacterial effect might  
 437 not only be related to the homogeneity and compatibility of the composites, since PE-GMA led  
 438 to lower performance in terms of mechanical resistance compared to PE-HEMA. The  
 439 understanding on the bactericidal action of phenolic compounds remains vague.<sup>28</sup> In the present  
 440 case, the lignin molecules being fully embedded in the matrix, a migrating phenomenon leading  
 441 to lignin's penetration through the cytoplasmic membrane is unlikely. Additionally, it was  
 442 recently shown that polyphenols exhibit different antibacterial activity on different type of  
 443 bacteria.<sup>29</sup> They could be very active against one strain and completely ineffective against  
 444 another and no clear correlation could be made with the class of polyphenols. However, the  
 445 dominant hypothesis of mechanism of action of polyphenols is that of an accumulation on  
 446 bacterial surface,<sup>30</sup> which would be linked to the polyphenol hydrophobicity.<sup>31</sup> Thus, it is  
 447 possible that the effect of the compatibilizer on the antimicrobial activity of the film results from  
 448 the interaction between the compatibilizer and lignin leading to the formation of a complex with  
 449 higher hydrophobicity than lignin alone.



450

451 *Figure 9. Bacterial reduction (in Log R) of S. Aureus of lignin containing films compared to a LDPE film*

## 452 Conclusion

453 The objective of this work was to assess the effect of two distinct compatibilizers on the  
 454 performances of PE-lignin blends, with mulching as targeted application. LDPE and PCR-PE were  
 455 successfully blended with a lignin sample containing a high phenolic content, allowing the  
 456 production of composites as molded parts and films. The results showed that the effect depends both  
 457 on the structure and content of the plasticizer. Depending on the test and the original PE resin, PE-  
 458 HEMA and PE-GMA performed differently but overall, PE-GMA proved to be a more effective  
 459 compatibilizer in terms of film quality and antimicrobial properties. The use of compatibilizers  
 460 enhanced the antioxidant properties which reached more than 3 h OIT when lignin was present at  
 461 20 wt% and beyond. The photo-permeability of the materials was also decreased, reaching a  
 462 transmittance lower than 5% throughout the whole measurement range (200 - 800 nm) when 20 wt%  
 463 of lignin was used in PCR. Additionally, good antibacterial properties were obtained on Gram-  
 464 positive bacteria when using PE-GMA as compatibilizer. While higher lignin contents led to a more  
 465 brittle material, processable films were achieved for both LDPE and PCR at 5 wt% lignin content. At  
 466 higher lignin contents, the compatibilizer failed to maintain some key properties such as the strain  
 467 at break in transversal direction, the puncture resistance and the overall processability of the material  
 468 became more difficult. However, it was demonstrated that lignin contents up to 30 wt% can be  
 469 potentially used in LDPE with an improvement of some materials' properties (antioxidant, UV  
 470 protection) beneficial for mulching film applications. Additionally, it was shown that it is possible to  
 471 use PCR made from different PE samples, instead of virgin plastic, while achieving similar

472 properties. These materials are thus promising candidates for mulching film application where PCR,  
473 which still lacks proper high-volume market applications, is more and more used.

#### 474 ASSOCIATED CONTENT

475 **Supporting information.** Experimental data, TGA, DSC, Haze, Gloss, mechanical properties  
476 (tensile, Izod impact, puncture resistance) and antibacterial tests of materials tested.

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##### 480 **Author Contributions**

481 The manuscript was written through contributions of all authors. All authors have given  
482 approval to the final version of the manuscript.

##### 483 **Notes**

484 The authors declare that they have no known competing financial interests or personal  
485 relationships that could have appeared to influence the work reported in this paper.

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#### 493 ABBREVIATIONS

494 HDPE: high density polyethylene; LDPE: low density polyethylene; LLDPE: linear low density  
495 polyethylene; PCR: Post-Consumer recycled; HEMA: 2-hydroxyethyl methyl acrylate; GMA: glycidyl  
496 methacrylate; RPM: Revolutions per minute; OIT: Oxidation Induction Time; NMR: Nuclear  
497 Magnetic Resonance; TGA: thermogravimetric analysis; DSC: differential scanning calorimetry;  
498  $\Delta H_m$ : enthalpy of melting;  $\Delta H_c$ : enthalpy of crystallization;  $T_c$ : crystallization temperature;  $T_m$ :  
499 melting temperature;  $X_c$ : degree of crystallinity ; TD: transverse direction; MD: machine direction

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