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1 **Organo-modified LDH fillers endowing multi-functionality to bio-**
2 **based poly(butylene succinate) : an extended study from the**
3 **laboratory to possible market**

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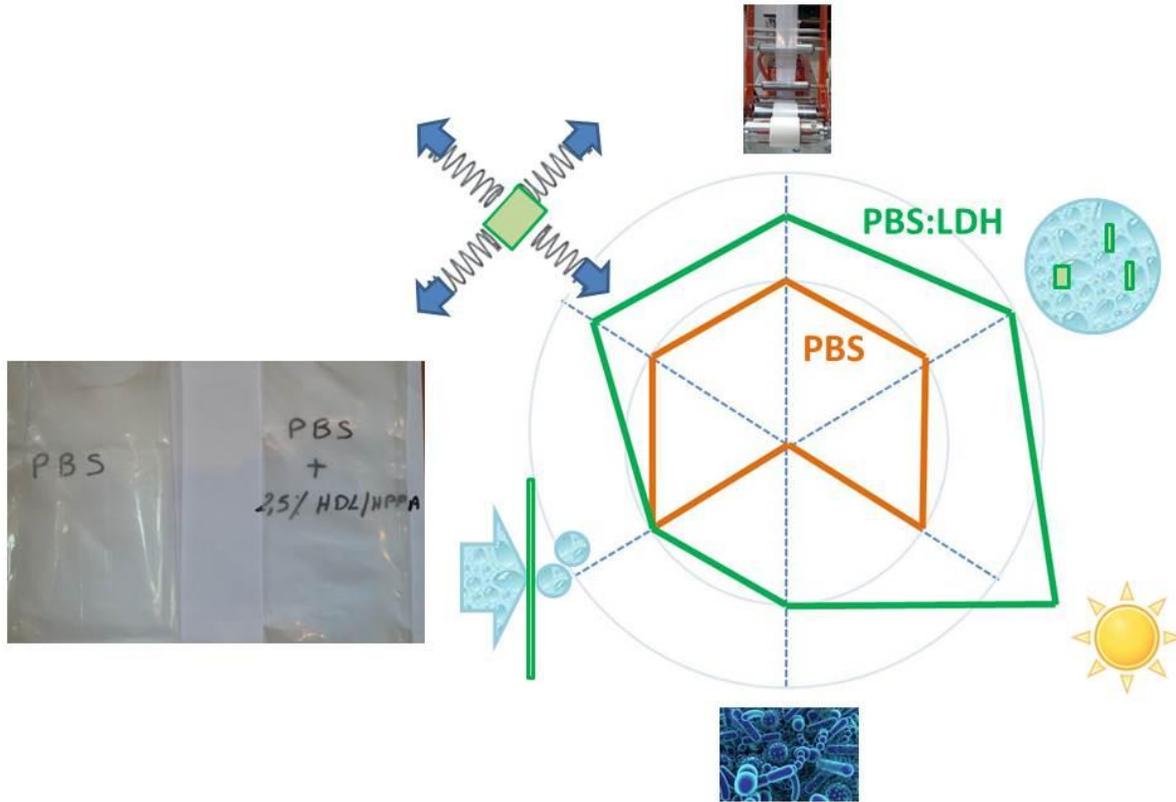
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Graphical Abstract



Highlights

23

24

25 Organo-modified LDH as filler for bio-based polyester

26 LDH hybrid filler endowing polymer with multi-functionality

27 Chain extension and stability against UV, hydrolysis and bacteria

28 Enhanced processability and durability of the polymer composite

29 Scale-up and applicability addressed

30

31

32

33 **Keywords:** layered double hydroxide; organo-modified filler; polymer nanocomposites;
34 rheology; antibacterial properties

35

36 ABSTRACT

37 Polybutylene succinate (PBS) were processed in melt extrusion by dispersion of organo-
38 modified layered double hydroxide (LDH). Depending on the organic anion interleaved into
39 LDH fillers (L-tyrosine (TYR), L-tryptophan (TRP), L-ascorbate (ASA) and 3-(4-
40 hydroxyphenyl)propionate (HPP)), it was possible to control and tune the properties of the
41 resulting PBS composites. Each LDH filler is found to act differently toward PBS, thus
42 modifying its viscoelastic properties (as expressed by a chain extending effect), its rate of
43 hydrolysis and photo-degradation or its antibacterial activity. The highest chain extending effect
44 was observed in the case of LDH with L-tryptophan, the worst – with L-ascorbate anion.
45 However, L-ascorbate anions interleaved into LDH present 100% activity in antibacterial
46 properties. A better compromise may be achieved when PBS is mixed with different LDHs such
47 as those combining HPP and ASA, making possible to target efficiently multi-properties such as
48 small rate of hydrolysis, photo-stability, biocide activity as well as chain extension, thus turning
49 to a multifunctional (bio)nanocomposites with new possible applications. Finally, a possible
50 scale-up is demonstrated on thin films.

51

52 1. INTRODUCTION

53 Polymers are one of the most important used materials in the world globalizing a whole
54 production estimated at 311 million tons in 2014 and expected to double again in 20 years.

55 About 26% of this total volume is used in packaging domains, for mostly single-use products
56 ([The New Plastics Economy, 2016](#)). Because still, a large majority is classical petroleum-based
57 polymers associated to their long-time natural degradation process, topical problems must be
58 faced concerning their collection, recycling or re-disposal (PSW - plastic solid waste) ([Al-Salem
59 et al., 2010](#)).

60 An alternative solution more sustainable may be the replacement of petroleum-based polymers
61 by eco-friendlier and renewable materials like bio-based aliphatic polyesters which are more and
62 more often used in products ([Demirkaya et al., 2015](#); [Rhim et al., 2013](#)). One of the most
63 promising member is poly(butylene succinate) (PBS), semi-crystalline polymer obtained by the
64 direct poly-condensation of succinic acid (bio-based) and butane-1,4-diol (partially bio-based).
65 Due to its thermal properties like glass transition temperature ($-34\text{ }^{\circ}\text{C}$) and relatively high
66 melting point (around $115\text{ }^{\circ}\text{C}$) close to some poly(olefins) such as poly(propylene), PBS can be
67 processed through usual extrusion, injection molding and thermo-forming processes, this is of
68 great interest since it guarantees direct industrial transfer. Moreover, via copolymerization with
69 other diols and dicarboxylic acids, or by the addition of organic and inorganic fillers, the
70 properties of PBS can be significantly improved, thus making PBS possible to replace classical
71 polymers in a wide range of applications ([Kim et al., 2005](#); [Gigli et al., 2016](#)).

72 In the last decades, a special attention has been paid to layered double hydroxides (LDHs), also
73 known as anionic clays or hydrotalcite-like materials. These materials can be described with the
74 general formula $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2](\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, where M^{II} is a divalent cation (like Mg, Zn,
75 Ni, Cu or Co) and M^{III} is a trivalent cation (like Al, Cr or Fe), and A^{n-} represents inorganic anion
76 such as NO_3^- , CO_3^{2-} or an organic anion. These metal cations $\text{M}(\text{OH})_6$ form the positively
77 charged layer by edge-sharing their octahedral, and with diverse charge-compensating anions

78 present in the interlayer space (Rives et al., 1999). By combining both cation and anion
79 versatilities, the resulting compositions are limitless in designing new hybrid LDH assemblies.
80 Often designed as toolbox, such organo-modified LDH may be adapted as nanofillers for
81 different types of polymer including bio-polymer to yield new polymer nanocomposites and thus
82 endowing them with enhanced target properties (Xie et al., 2016; Totaro et al., 2017; Coelho et
83 al., 2012).

84 In the present paper, a family of multifunctional PBS nanocomposites adopting organo-
85 modified Mg-Al LDHs as filler are characterized, that may be potentially used in packaging
86 domains. In the same vein, Costantino et al. have demonstrated the active antimicrobial activity
87 of benzoate organic derivatives intercalated into Zn₂Al and dispersed into poly(ϵ -caprolactone)
88 (Costantino et al., 2009). Here, the LDHs nanofillers were obtained by the straightforward co-
89 precipitation method with anions coming from 3-(4-hydroxyphenyl)propionate (HPP), L-
90 ascorbate (ASA) and amino acids: L-tyrosine (TYR) and L-tryptophan (TRP). Such selection is
91 explained by the fact that HPP interleaved molecules provide an effective chain extender toward
92 PBS when hosted by Mg-Al LDH structure (Totaro et al., 2017) as well as developing some
93 antioxidant and antibacterial activities (Sun et al., 2016). The other candidates, ASA molecule
94 (called vitamin C) is known as an antioxidant and free radical scavenger. Its key role in the
95 body's life includes to protect the immune system (destroy tumour cells), the cardiovascular
96 system (support the fat metabolism) (Aisawa et al., 2007), while the amino acids TYR and TRP
97 may supply anti-UV properties and polymer chain extension (Coelho et al., 2012).

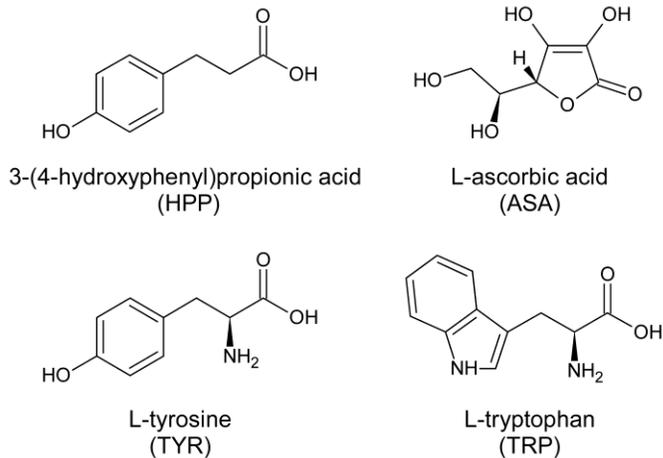
98 Having in mind such combination of properties potentially available, the synthesized LDHs
99 assemblies were dispersed into PBS by melt extrusion process. The resulting PBS composites
100 were scrutinized to determine the chain extension effect, photo- and hydro-stability as well as the

101 antibacterial activity against *Escherichia coli* and *Staphylococcus aureus*. Some trends are
102 featured in terms of correlation between the rheological properties (Newtonian viscosity η'_0
103 associated to the chain extension effect) and the antibacterial properties, as well as between η'_0
104 before and after photo-aging and the hydrolysis processes. This comprehensive analyses should
105 help to underline the multifunctional properties of the obtained PBS nanocomposites with
106 potential use for food packaging applications and others. Indeed, a scale-up of 30,000 g of a
107 composite Mg₂Al/HPP : PBS (2 wt. % dry filler) is easily achieved, however in adopting the
108 «slurry» method for a better dispersion of state, thus yielding to thin film that is found to exhibit
109 similar modulus, maximum at strain and water vapor transmission rate (WVTR), but extension
110 as well as tearing greater than PBS free of filler.

111

112 2. EXPERIMENTAL SECTION

113 **2.1. Materials.** Sodium hydroxide, aluminium nitrate Al(NO₃)₃·9H₂O, magnesium nitrate
114 Mg(NO₃)₂·6H₂O, sodium nitrate NaNO₃ and the guest molecules: L-tyrosine (TYR), L-
115 tryptophan (TRP), L-ascorbic acid (ASA) and 3-(4-hydroxyphenyl)propionic acid (HPP) were
116 purchased from Sigma-Aldrich Chemical. PBS (PBE003) and PuralMg61 were purchased from
117 NaturePlast and Sasol Germany GmbH, respectively. Plate Count Agar (PCA), Nutrient Broth
118 (NB) were supplied from Oxoid, Basingstoke, UK and phosphate buffer solution was purchased
119 by Merck, Darmstadt, Germany. All the materials were reagent grade and used as received. The
120 molecular structures of organic quest molecules are presented at **Scheme 1**.



121

122 **Scheme 1.** The organic guest molecular structures.

123 **2.2. Synthesis of layered double hydroxides.** The host substances Mg-Al LDHs with general
 124 formula $Mg_2Al(OH)_6[A] \cdot 2H_2O$ (A = HPP, ASA, TYR or TRP) were prepared using so-called
 125 co-precipitation method with an initial metal cation feed of Mg:Al of 2 and A:Al of 4.
 126 $Al(NO_3)_3 \cdot 9H_2O$, and $Mg(NO_3)_2 \cdot 6H_2O$ were mixed with milliQ water (100 mL) and added
 127 dropwise to the 50 mL solution of organic guest in water. The reaction was carried out with
 128 vigorous stirring and under nitrogen atmosphere to avoid contamination by carbonate during 3.5
 129 h. The pH was kept constant ($9.5-11.0 \pm 0.1$) with the addition of NaOH solution. After 3.5 h,
 130 the salts addition was finished and the reaction mixture was aged for next 3.5 h at room
 131 temperature. The final products were centrifuged, washed with deionized water and dried at 40
 132 °C in vacuum-oven for 24 h.

133 **2.3. Melt compounding.** PBS/LDH composites were obtained by a melt extrusion process in a
 134 twin screw extruder Hakke MINILAB microcompounder (Thermo Electron Corporation). The
 135 process was performed at 120 °C, with a roller speed of 100 rpm over 5 min.

136 **2.4. Grinding-homogenization process.** Homogenized LDH fillers and PBS/LDH composites
 137 were grinded in Retsch CryoMill machine. Prior to dispersion, LDH fillers were sieved to obtain
 138 fraction with particles size below 50 μm .

139 **2.5. Film making.** PBS/LDH composite films with thickness about 90–100 μm , used in
140 hydrolysis and photodegradation studies, were prepared by compression moulding. About 0.5 g
141 of composites were placed between two Teflon sheets for one minute under 100 bars at 120 $^{\circ}\text{C}$.

142 **2.6. Hydrolysis procedure.** PBS and PBS/LDH composite films were placed into glass pots
143 with deionized water, purged with nitrogen and closed in the dark in an oven at 35 and 50 $^{\circ}\text{C}$.
144 These processes were performed two times, separately for succinic acid analysis (by ionic
145 chromatography) and for rheological measurements.

146 **2.7. Photodegradation procedure.** PBS and PBS/LDH composite films were placed on a
147 rotating carousel in a SEPAP 12/24 chamber from ATLAS. This apparatus is equipped with four
148 400 W mercury lamps with $\lambda > 300$ nm light and allows for study the accelerated photo-
149 degradation of polymer. The conditions used in experiments were air atmosphere and 60 $^{\circ}\text{C}$.

150 **2.8. Antibacterial analysis.** The antimicrobial activity of LDHs and PBS composites was
151 assessed by evaluating the survival of bacterial cells (*Escherichia coli* ATCC 11105 and
152 *Staphylococcus aureus* ATCC 6538) in contact with samples. The bacterial culture obtained in
153 NB Medium and aerobic atmosphere for 16 h at 37 $^{\circ}\text{C}$ was next centrifuged at 7000 rpm for 10
154 min, washed in sterile phosphate buffer solution and re-suspended in the same buffer in order to
155 obtain about 10^5 colony forming unit per milliliter (CFU mL^{-1}).

156 The experiments on both LDHs and PBS composites were performed using 50 mg of sieved
157 samples placed into an Eppendorf with 500 μl of cells (10^5 CFU mL^{-1} in phosphate buffer) at 23
158 ± 1 $^{\circ}\text{C}$, gently shaken at 30 rpm for 24 h. After the incubation period, each sample was diluted
159 (1:10) and the dilutions were plated on PCA medium. After incubation of the plates at 37 $^{\circ}\text{C}$ for
160 24 h, the number of colonies corresponding to the number of viable cells was determined, after
161 averaging using triplicates, through a modification of the equation as follow (Lala et al., 2007):

185 thermal history of samples was deleted and 2nd scan was performed, by heating from -60 °C to
186 150 °C at 10 °C/min. The glass transition temperature (T_g), the melting temperature (T_m) and the
187 enthalpy of fusion (ΔH_m) were measured from 2nd scan. T_g was taken as the midpoint of the heat
188 capacity increment associated with the glass-to-rubber transition. The crystallization temperature
189 (T_c) and the enthalpy of crystallization (ΔH_c) were measured during the cooling scan.

190 Thermogravimetric analysis (TGA) of LDH fillers and composites, was performed in air
191 atmosphere (gas flow 30 mL/min) using a Perkin Elmer TGA7 apparatus. The temperature range
192 from 50 to 800 °C and heating rate 10 °C/min were applied. The onset degradation temperatures
193 (T_{onset}) were taken from the intersections of the tangents of the initial points and the inflection
194 points. The 10% mass loss temperatures (T^{10}_D) were also measured.

195 The melt rheological properties of the polymer composites were measured in oscillatory
196 frequency sweep mode at 120 °C, using a dynamic mechanical spectrometer (ARES Rheometric
197 Scientific T&A Instruments) equipped with two parallel plate-holders. Diameter of both plates
198 was 8 mm and the gap during measurement was 1 mm. In all cases, the range of frequency
199 sweeps was from 0.1 to 100 rad/s and the oscillatory shear stress amplitude was checked to
200 perform measurement inside the linear viscoelastic domain. The storage modulus (G'), loss
201 modulus (G'') and $\tan \delta$ (ratio of G' and G'') were monitored automatically against frequency.

202 The concentration of succinic acid was measured by ionic chromatography method, using a
203 Thermo Scientific ICS5000 apparatus with conductivity detector, self-regenerating suppressor
204 (SRS) and columns: AS18 2x250 and AG18 2x50 (guard-column). Samples (250 μ L) were
205 analyzed at 40 °C, with a flow rate of 0.25 mL/min and run time 35 min. The initial eluent
206 concentration during analysis was changed according to T_0 : 10, T_4 : 11, T_{11} : 17, T_{21} : 19.5 and
207 $T_{23.1}$: 10 mM KOH /L.

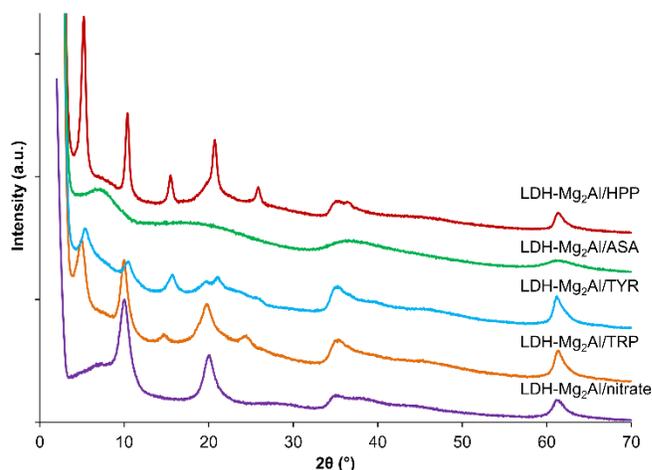
208 **2.10. Scale-up and characterization of the obtained thin films.** LDH/HPP material was
209 scaled-up to yield about 600 g of powder mass. To avoid any particle aggregation during the
210 polymer processing, the filler LDH/HPP was mixed with glycerol and water in a mass ratio
211 LDH/HPP : glycerol : water of 1:1:3. The mixing was performed in an Ultra Turax during 45' at
212 8,000 rpm. Extrusion was performed by a twin-screw Clextral BC21 and the slurry was
213 incorporated by pumping (DKM, feeding zone Z2/Z3), and feeding speed of 10,000 g/h for PBS
214 granulates and 750 g/h for LDH slurry, this to reach a filler loading of 2.5 wt. %. The extruded
215 polymer and filler was dried during 2 h at 70°C. The resulting film thickness, performed with a
216 monolayer extrusion line (EuRexMa XTR20) was of 35 µm and 25 µm for PBS free of filler.
217 Barrier effect at the water vapor (WVTR) was measured using the norm EN NF ISO 2528 at 38
218 °C and 90% humidity rate (HR).

219

220 **3. RESULTS AND DISCUSSION**

221 **3.1. LDH fillers characterization.** The organo-modified Mg₂Al/A LDH assemblies (A = HPP,
222 ASA, TYR or TRP) subsequently used in PBS nanocomposites, were prepared by co-
223 precipitation method with intercalation of organic molecules: 3-(4-hydroxyphenyl)propionate
224 (HPP), L-ascorbate (ASA) anions and amino acids: L-tyrosine (TYR) and L-tryptophan (TRP).
225 They present structural features characteristic of layered system as shown by their XRD patterns
226 (**Fig. 1**) together with LDH/nitrate used as reference.

227



228

229 **Fig. 1.** XRD patterns of Mg_2Al/A ($A = HPP, TRP, TYR, ASA, nitrate$) organo-modified LDHs.

230 Indeed, LDH/A structural host guest assemblies present XRD patterns with narrow and
 231 symmetric ($00l$) harmonic peaks at low angle. They correspond to the basal spacing (d -value) and
 232 indicate higher order reflections, resulting from a high degree of platelets stacking. This is not
 233 the case for Mg_2Al/ASA that exhibits wide reflection peaks. Some authors suggest, that the
 234 molecules ASA may be arranged horizontally between LDH sheets and with the hydroxyl groups
 235 (OH^-) co-intercalated as well. The latter fact may contribute to the ill-organized stacking
 236 arrangement ([Aisawa et al., 2007](#)).

237 It can be noticed, that $Mg_2Al/nitrate$ LDH shows basal reflections at low 2θ angles leading a
 238 d_{001} -value of 0.84 nm. The uptake of organic guest into LDH structure causes an increase of the
 239 interlayer space. The chemical composition as well as the cell parameters are summarized (**Table**
 240 **1**).

241

242 **Table 1.** Chemical compositions and cell parameters of the organo-modified LDHs

Sample	Chemical composition ^{a)}	Interlayer	$c=3c'$	d_{110}	$a=2d_{110}$
--------	------------------------------------	------------	---------	-----------	--------------

		distance $c' = d_{003}$ (nm) ^{b)}	(nm) ^{c)}	(nm) ^{d)}	(nm) ^{e)}
PuralMg61	$[\text{Mg}_{0.61}\text{Al}_{0.39}(\text{OH})_2](\text{CO}_3^{2-})_{0.195} \cdot 0.46\text{H}_2\text{O}$	0.77	2.31	0.152	0.304
Mg ₂ Al/nitrate	$[\text{Mg}_{0.66}\text{Al}_{0.33}(\text{OH})_2](\text{NO}_3^-)_{0.37} \cdot 0.74\text{H}_2\text{O}$	0.84	2.52	0.151	0.302
Mg ₂ Al/HPP	$[\text{Mg}_{0.66}\text{Al}_{0.33}(\text{OH})_2](\text{HPP}^-)_{0.23} \cdot 0.19\text{H}_2\text{O}$	1.68	5.04	0.151	0.302
Mg ₂ Al/ASA	$[\text{Mg}_{0.66}\text{Al}_{0.33}(\text{OH})_2](\text{ASA}^-)_{0.36} \cdot 0.22\text{H}_2\text{O}$	1.24	3.72	0.151	0.302
Mg ₂ Al/TYR	$[\text{Mg}_{0.66}\text{Al}_{0.33}(\text{OH})_2](\text{TYR}^-)_{0.31} \cdot 0.19\text{H}_2\text{O}$	1.66	4.98	0.151	0.302
Mg ₂ Al/TRP	$[\text{Mg}_{0.66}\text{Al}_{0.33}(\text{OH})_2](\text{TRP}^-)_{0.32} \cdot 0.15\text{H}_2\text{O}$	1.80	5.40	0.151	0.302

243 a) Anion and water content were determined by TGA (i.e. molar mass).

244 b) Determined by the 003 reflection in XRD analysis.

245 c) Total thickness of the brucite-like layers and the interlayer distance.

246 d) Determined by the 110 reflection in XRD analysis.

247 e) Lattice parameter related to the cation-cation distance.

248

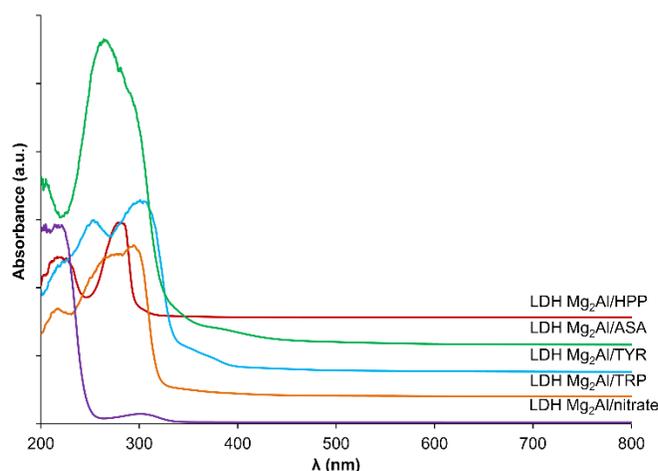
249 The cell parameter **a**, calculated from the position of the reflection (*110*), indicates any deviation
 250 from the stoichiometry with respect to the structural references (here Mg-Al/nitrate) (Cavani et
 251 al., 1991). For the obtained O/I LDHs, a value of **a** is 0.302 nm. In comparison to the nitrate
 252 reference, this value confirms a constant cation ratio Mg:Al of 2. It is worth to mention the
 253 absence of contamination by LDH/carbonate phase.

254 FTIR spectra of Mg₂Al LDH hybrids are presented in **Fig. S1**. The observed bands confirm the
 255 presence of anions and the position of the vibration bands agrees with literature (Totaro et al.,
 256 2017; Gao et al., 2013; Wei et al., 2005).

257 The UV-absorbing properties of Mg-Al LDHs are presented in **Fig. 2**. The nitrate-inorganic
 258 derivative, which is used as reference, presents practically no absorption in the UV range. When
 259 the organic molecules are inserted into LDH structure, the absorption increases significantly,

260 especially in the case of ASA and amino acid TRP and TYR, with the maximum absorption of
261 266, 296 and 303 nm, respectively. In the case of Mg₂Al/HPP, a narrower absorption range with
262 maximum 281 nm is observed. The presented spectra indicate, that these organo-modified Mg-Al
263 LDHs should be effective as potential UV-absorbers. Their UV-stabilizing effect on PBS will be
264 addressed in a next section.

265

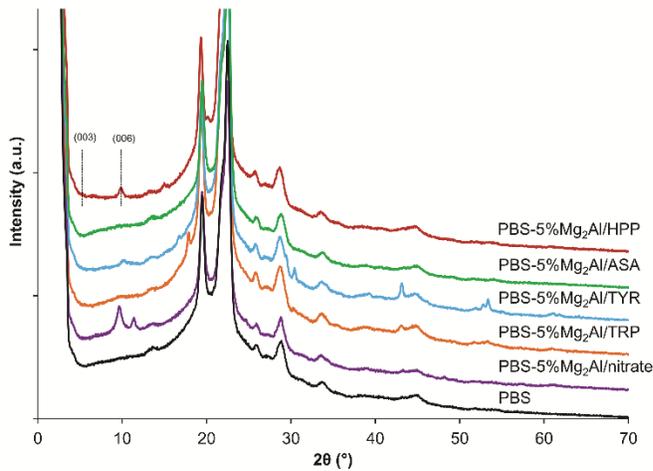


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267 **Fig. 2.** Diffuse reflectance UV-vis spectra (Kubelka–Munk functions) of organo-modified Mg-Al
268 LDHs.

269

270 **3.2. PBS-LDH composites characterization.** PBS nanocomposites were prepared by melt
271 extrusion with the addition of synthesized Mg-Al LDHs in amount between 2.5 to 10 wt. %. The
272 fillers were used individually or as mixture in combination with Mg₂Al/HPP (1:1) which is
273 known as a chain extender in PBS composites (Leroux et al., 2017; Totaro et al., 2017). PBS
274 nanocomposites with 5 wt. % of organo-modified Mg₂Al LDHs and its nitrate reference are
275 characterized by XRD and the associated patterns displayed in **Fig. 3** (summarized in **Fig. S3** for
276 loading of 10 wt. %).



278

279 **Fig. 3.** XRD patterns of PBS and PBS nanocomposites with 5 wt. % of Mg-Al organo-modified
 280 LDH fillers.

281

282 At first, some reflections are due to the semi-crystalline structure of PBS. Indeed in the 2θ range
 283 between 18 and 35° , the following reflections are visible and assigned to (020) (021) (110) (111)
 284 of PBS crystal in monoclinic symmetry (Yoo and Im., 1999). From those reflections, neither
 285 their location nor their relative intensity is modified after the incorporation of LDH-based filler.
 286 This indicates that the filler loading does not affect the PBS molecular crystal. Secondly, the
 287 harmonic peaks arising from the layered structure of LDH are not observed anymore, except for
 288 LDH/HPP, for which the (003) and (006) are depicted at 5 and 10 wt. % (Fig. 3 and Fig. S3).
 289 The basal reflection (003) is also observed for LDH/nitrate. For Mg₂Al/HPP, the observation of
 290 some layered structure remaining after extrusion is not surprising since the LDH structure is
 291 initially extensively stacked as observed by its narrow (00 l) basal reflections, *i.e.* its large
 292 coherence length along the stacking direction. The absence of harmonic peaks for the other
 293 compositions suggests an intimate mixture between its layered structure and the polymer chain.

294 One cannot discard the possible presence of carbonate contamination within LDH in the case of
 295 LDH/nitrate loaded as 5 wt. % and of Mg₂Al/HPP as 10 wt. % (**Fig. S3**). As the LDH fillers are
 296 initially free of carbonate contamination (Fig. 1), it means that the contamination is occurring
 297 during the thermal pretreatment or the exposure to air before their dispersion into PBS and/or
 298 during the extrusion process in temperature.

299 The calorimetric and thermogravimetric data for PBS nanocomposites with Mg-Al LDHs are
 300 summarized in **Table 2**, and TGA thermograms of nanocomposites with 5 wt. % of LDHs are
 301 shown in **Fig. 4** as example. TGA and DTGA traces for the PBS nanocomposites (with the other
 302 filler loadings 2.5 and 10 wt. % and mixtures of LDHs) are shown in the ESI (**Fig. S2**).

303 **Table 2.** TGA and DSC results of melt blended PBS nanocomposites with Mg-Al LDHs filler.

Sample	T _{onset} (°C) ^{a)}	T ¹⁰ _D (°C) ^{a)}	Res. mass (%) ^{a)}	T _C (°C) ^{b)}	ΔH _C (J/g) ^{b)}	T _g (°C) ^{c)}	T _m (°C) ^{c)}	ΔH _m (J/g) ^{c)}
PBS pure	385	362	0.7	85	63	-31	115	47
PBS-5%Mg ₂ Al/nitrate	360	327	3.3	85	58	-31	115	48
PBS-5%Mg ₂ Al/HPP	369	345	3.3	85	54	-32	114	50
PBS-10%Mg ₂ Al/HPP	363	338	5.0	85	56	-33	114	50
PBS-2.5%Mg ₂ Al/ASA	370	350	1.8	84	55	-29	116	46
PBS-5%Mg ₂ Al/ASA	371	347	3.4	86	62	-30	116	49
PBS-10%Mg ₂ Al/ASA	368	341	5.1	86	52	-29	115	43
PBS-2.5%Mg ₂ Al/TYR	379	354	1.5	88	62	-29	115	49
PBS-5%Mg ₂ Al/TYR	376	351	2.6	87	58	-29	115	41
PBS-10%Mg ₂ Al/TYR	372	344	4.9	84	55	-31	115	43
PBS-2.5%Mg ₂ Al/TRP	371	351	1.3	86	56	-26	115	47
PBS-5%Mg ₂ Al/TRP	367	349	2.8	85	56	-33	114	46

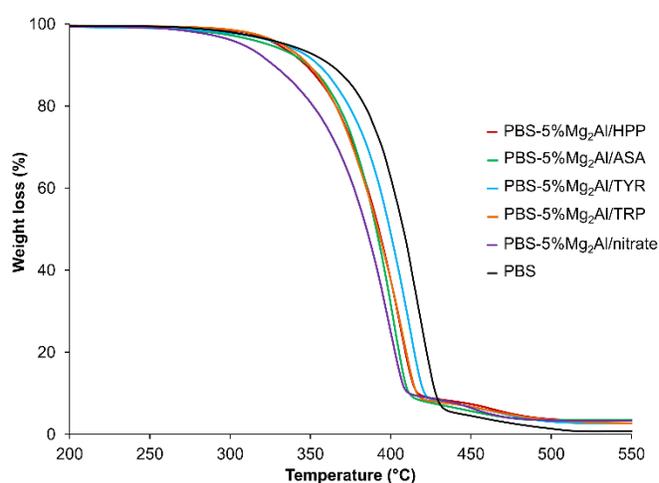
PBS-10%Mg ₂ Al/TRP	371	357	4.5	83	50	-33	114	33
PBS-10%Mg ₂ Al/HPP:ASA	360	335	2.9	85	53	-33	115	46
PBS-10%Mg ₂ Al/HPP:TYR	361	337	4.9	84	57	-31	115	48
PBS-10%Mg ₂ Al/HPP:TRP	357	337	4.1	84	53	-30	114	43

304 a) Determined by TGA at 10 °C/min in air.

305 b) Determined by DSC during the cooling scan from the melt at 10 °C/min.

306 c) Determined by DSC during the 2nd heating scan at 10 °C/min.

307



308

309 **Fig. 4.** TGA traces of PBS and PBS nanocomposites with 5 wt. % of Mg-Al organo-modified
310 LDHs.

311 All nanocomposites exhibit some lower thermal stability than pure PBS, that is characterized by
312 a decrease in T_{onset} (initial temperature of degradation process) and in T^{10}_{D} (temperature at which
313 the material lose 10% of weight). This trend is also observed with increasing the LDH amount.

314 Only in the case of PBS with 10 wt. % of Mg₂Al/TRP LDH, an opposite effect and higher T_{onset}
315 and T^{10}_{D} are observed than for 5 wt. % amount, but still bellow PBS alone. This is probably due
316 to a stronger affinity of the platelets toward the cross-linking reactions with PBS. This was

317 previously noticed for PBS-Mg₂Al/TRP composites but obtained through in-situ polymerization
318 process (Totaro et al., 2018).

319 A complete decomposition occurs in the range 300–450 °C. It is in accordance with the literature
320 (Totaro et al. 2018; Wei et al., 2012) and can be explained by degradation process of PBS, this
321 catalyzed by the metal ions inside the layers as well as the water molecules released during the
322 decomposition.

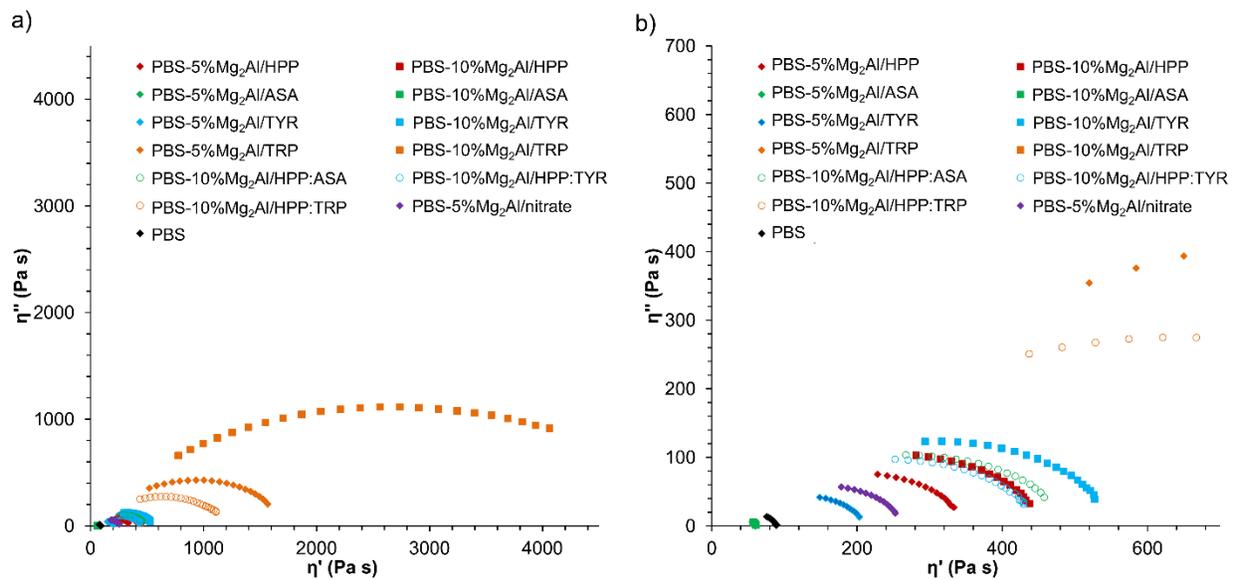
323

324 **3.3. Chain extending effect.** It is well known that additives may endow polymers with
325 required properties to reach possible application. One of the basic characteristic is the molecular
326 weight and the associated viscoelastic behavior, which can be modified by addition of
327 plasticizers (smaller molecular weight) or chain extenders (higher molecular weight). The latter
328 can also be used during processing polymer condensation as illustrated by PET to avoid negative
329 effect of thermo-hydrolysis reaction during thermomechanical processing (Bimestre et al., 2012).

330 The effect of synthesized LDH fillers on the molecular weight evolution is here examined. It is
331 monitored by rheology in the molten state and described according to the so-called Cole-Cole
332 plot, commonly adopted to scrutinize any variations in the complex viscosity components. By
333 plotting the imaginary viscosity (η'') versus real viscosity (η'), a circle arc in the complex plane
334 is observed (Friedrich et al., 1992). Indeed, such representation highlights clearly the polymer
335 composites molecular evolution by fitting the Cole-Cole depressed semi-circle and its
336 extrapolation to the x-axis (η' at $\eta'' = 0$), the Newtonian zero-shear viscosity η'_0 , which reflects
337 the change in the molecular mass, calculated according to (Mark-Houwink equation, 2007)

338
$$\eta'_0 \propto M_w^a \quad (2)$$

339 The synthesized Mg-Al LDHs were loaded to PBS matrix in 2.5–10 wt. %. The mixtures of
 340 LDHs including Mg₂Al/HPP with another LDH hybrid filler in mass ratio 1:1, are also prepared
 341 to possibly tune PBS towards multi-properties. The effect of using nanofillers on PBS chain
 342 extension is presented as $\eta'' - \eta'$ Cole-Cole plots (**Fig. 5**) and the resulting values of the
 343 Newtonian zero-shear viscosity are summarized in **Table 3**.
 344



345
 346 **Fig. 5.** Cole-Cole plots of (a) PBS and PBS nanocomposites with Mg-Al organo-modified LDH
 347 fillers, (b) zoom region in the lower values of viscosity.

348
 349 **Table 3.** Newtonian zero-shear viscosity η'_0 for PBS composites as a function of the loadings
 350 using Mg-Al organo-modified LDH fillers.

PBS nanocomposites	η'_0 (Pa s) in dependent of LDH amount (wt. %)			
	0	2.5	5	10
PBS pure	90			
PBS-Mg ₂ Al/nitrate	274			

PBS-Mg ₂ Al/HPP		365	475
PBS-Mg ₂ Al/ASA	96	80	82
PBS-Mg ₂ Al/TYR	91	218	580
PBS-Mg ₂ Al/TRP	388	1815	5356
PBS-Mg ₂ Al/HPP:ASA			515
PBS-Mg ₂ Al/HPP:TYR			470
PBS-Mg ₂ Al/HPP:TRP			1269

351

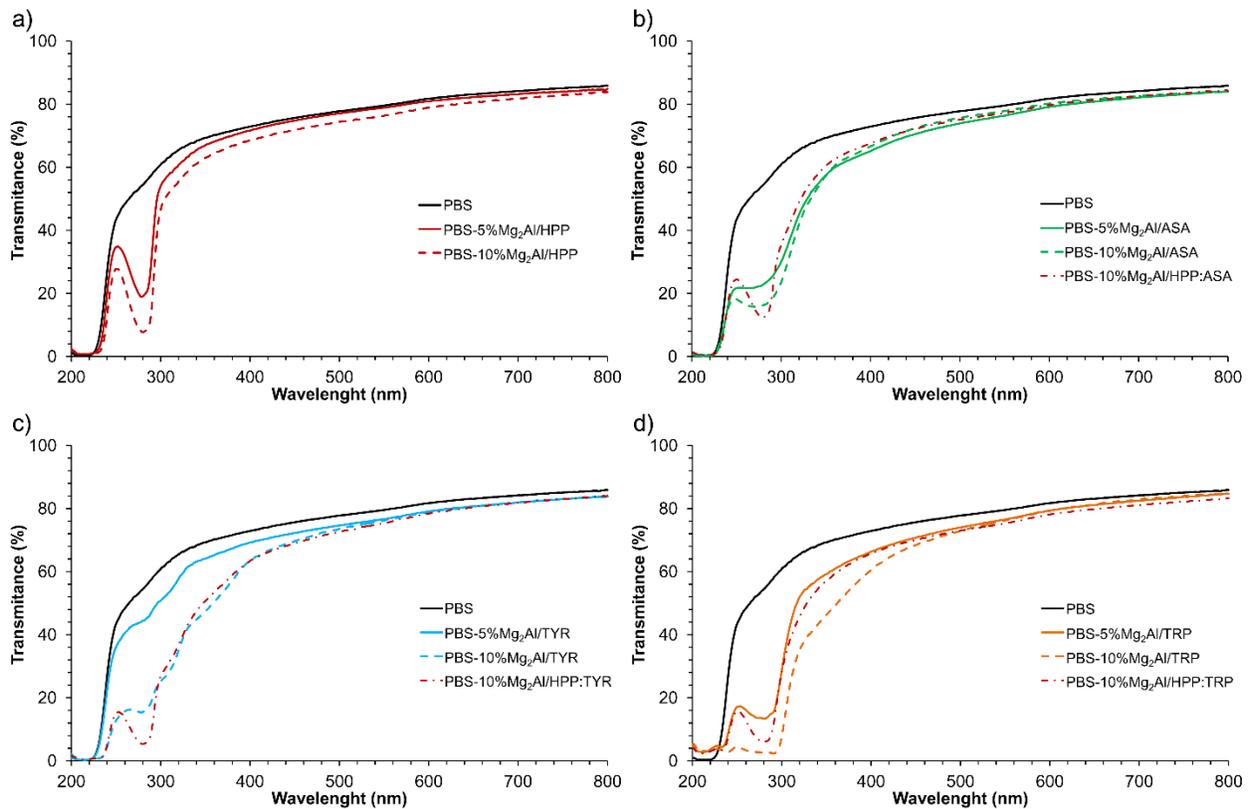
352 One of the best results is obtained for Mg₂Al/TRP; quantitatively, loaded as low as 2.5 wt. %,
 353 the Newtonian zero-shear viscosity is similar to Mg₂Al/HPP, however, using twice the amount. It
 354 is worth to mention that the response in η'_0 is not linear as a function of mass loading, since an
 355 increase of one order for η'_0 is observed at 10 wt. % between both fillers. The influence of
 356 Mg₂Al/TYR is weaker, and in the case of Mg₂Al/ASA, a plasticizing effect is observed. Such
 357 differences between LDHs may result from the chemical structures and from the tethered organic
 358 molecules as well as the state of dispersion.

359

360 **3.4. Photo-stability of PBS nanocomposites.** PBS and PBS nanocomposites with Mg-Al
 361 LDHs were exposed on UV irradiation in accelerated ageing chamber under aerobic conditions
 362 at 60 °C. Since Mg-Al organo-modified LDHs exhibit UV absorption (**Fig. 2**), their derivative
 363 PBS composites are expected to be UV-stabilized. The UV-vis transmittance spectra are
 364 presented in **Fig. 6**. A better performance as a UV stabilizer is shown in the case of the addition
 365 of 10 wt. % of Mg₂Al/TRP into PBS. The transmittance decreases practically to zero in the UV-
 366 C range (100–280 nm) and below 40% in the UV-B range (280–315 nm). For the other PBS
 367 composites, the efficiency in UV absorption is little less. It is worth to mention that the UV

368 absorption is not filler loading-dependent and after a certain mass loading (5 wt. %), the effect is
369 constant.

370



371

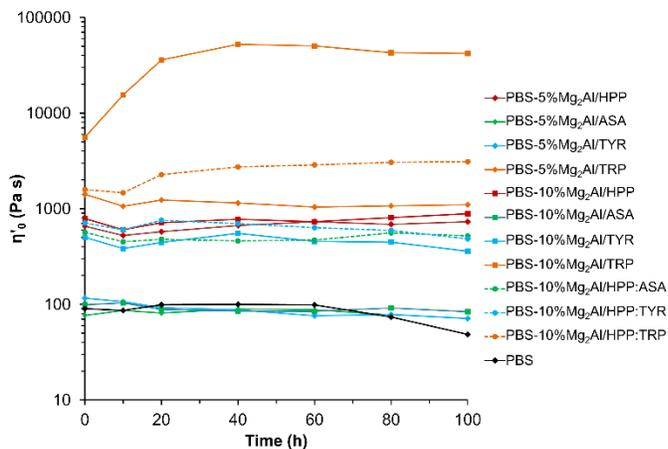
372 **Fig. 6.** UV-vis transmittance spectra of PBS and PBS composites with Mg-Al organo-modified
373 LDHs: (a) Mg₂Al/HPP, (b) Mg₂Al/ASA, (c) Mg₂Al/TYR and (d) Mg₂Al/TRP.

374

375 The variation of Newtonian viscosity η'_0 during exposure on UV radiation is presented in **Fig.**
376 **7.** Pure PBS shows UV-resistance for the first 60 h, then it begins to degrade rather quickly. The
377 addition of Mg₂Al/TYR LDH turns out to be completely ineffective, regardless of the amount
378 used, a slow decrease in viscosity (effect of the photo-degradation) is observed. The other LDH
379 hybrids act as UV-stabilizers during the time period. In the case of composites with 10 wt. % of
380 Mg₂Al/TRP and Mg₂Al/HPP:TRP LDHs mixture, which have the highest Newtonian viscosity, a

381 further increase in η'_0 is observed, probably due to additional crosslinking reactions. The cross-
382 linking phenomenon in the presence of LDH modified with amino acids like TRP, has recently
383 been depicted (Totaro et al., 2018).

384



385

386 **Fig. 7.** Evolution of Newtonian zero-shear viscosity η'_0 (in logarithmic scale) versus time for
387 PBS and PBS-Mg-Al LDH composites, during photo-aging at 60 °C.

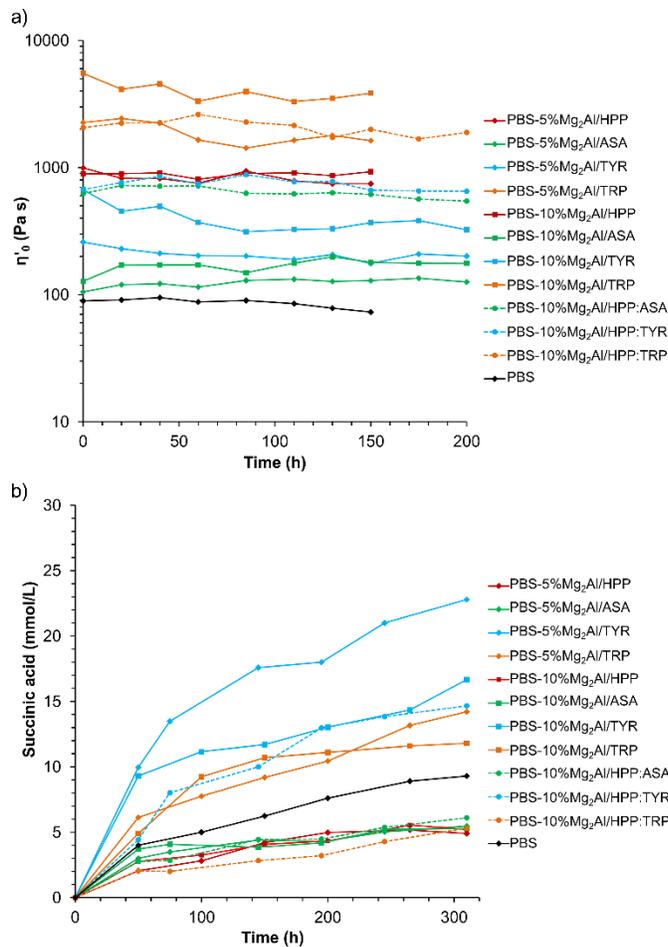
388

389 UV-vis transmittance spectra of PBS and its nanocomposites with 5 wt. % of Mg-Al LDH,
390 before and during UV radiation, are presented in **Fig. S4**. Pure PBS does not present any UV-
391 sensitive functional groups, and its transmittance spectra are not changed during the process. The
392 dispersion of Mg-Al LDHs into PBS decreases the transmittance band at about 300 nm, however
393 a lower effect is observed for composite with TYR compound. When the samples are irradiated,
394 the transmittance is changed. For the PBS-Mg₂Al/ASA composite, it increases during all time of
395 radiation, while for the other composites a decrease in transmittance is observed during a first
396 period (10–40 h), depending of organic molecule used (TRP, HPP) and then it increases again.
397 This phenomenon may be caused by the transformation of molecules within the LDH structure or
398 by their interaction with the polymer matrix.

399 Significant changes caused by UV on some of the PBS nanocomposites have been also
400 registered using fluorescence spectroscopy (**Fig. S4**), similar to the decrease of UV
401 transmittance, described before.

402 **3.5. Hydrolysis of PBS nanocomposites.** Hydrolysis of PBS and PBS-Mg-Al LDH
403 composites is performed at 35 and 50 °C. The reaction progress is monitored by both; the
404 evolution of Newtonian zero-shear viscosity and the release of succinic acid during hydrolysis.
405 When the process is performed at 35 °C, the Newtonian zero-shear viscosity seems to be quite
406 stable (**Fig. 8**). Only for pure PBS and composites with 5 and 10 wt. % of Mg₂Al/TRP and
407 Mg₂Al/TYR LDHs, the viscosity decreases, however in the case of composites, after 80 h, the
408 value of viscosity is stabilized in contrast to pure PBS.

409



410

411 **Fig. 8.** (a) Evolution of Newtonian zero-shear viscosity (in logarithmic scale) and (b) succinic
 412 acid concentration vs time for PBS and PBS-Mg-Al LDH composites, during hydrolysis at
 413 35 °C.

414

415 These results can be confirmed by the observation of succinic acid concentration measured by
 416 ionic chromatography (**Fig. 8b**). The succinic acid is released most intensively (10–22 mmol/L
 417 after 310 h) for all composites with Mg₂Al/TYR LDH and Mg₂Al/TRP LDH used alone. For the
 418 other composites, the final concentration is lower of about 1.5 times than for pure polymer and
 419 does not exceed 6 mmol/L. The significant viscosity decrease observed for composites with
 420 Mg₂Al/TRP and Mg₂Al/TYR during the first hours, is most probably caused by hydrolysis

421 reaction of the polymer. These results are promising for composites with HPP and ASA Mg-Al
422 LDHs. It is also interesting to note that the release in succinic acid is not correlated to the
423 solubility of the anions, of 330, 2.71, 1.4, 11.4 and 58 g/L for ASA, HPP, TYR, TRP and
424 succinic acid, respectively. Counter-intuitively, the greater release of succinic acid is for the less
425 soluble anions such as TYR and TRP, while the smaller release is for the highly soluble ASA
426 anions.

427 The hydrolysis experiment is repeated at 50 °C and at this temperature, a higher rate of
428 hydrolysis is observed (**Fig. S6 a and b**). Once again the composites containing Mg₂Al/TRP and
429 Mg₂Al/TYR LDHs seem to be the less resistant to the aqueous environment. The Newtonian
430 zero-shear viscosity of composites with 5 and 10 wt. % of fillers, after 200 h decreases by 78 and
431 83% for Mg₂Al/TRP and 67 and 52% for Mg₂Al/TYR LDHs, respectively. Even in the case of
432 Mg₂Al/HPP LDH, which is supposed to act as an efficient chain extender, the final η'_0 was 33
433 and 39% of its initial values. However, the temperature 50 °C is relatively high for packaging
434 materials and the degradation of PBS and LDH fillers is not surprising. The succinate anions
435 content in water (**Fig. S6 b**) is about two times higher than for processes performed at 35 °C. The
436 highest concentration is detected as previously for Mg₂Al/TYR and 10 wt. % Mg₂Al/TRP PBS
437 composites, with 38 to 48 mmol/L respectively after 310 h of immersion, while the value is
438 about 22 mmol/L for PBS free of filler. The best results (lower content of succinate anions) are
439 obtained for composites with 5 wt. % of Mg₂Al/HPP and those containing Mg₂Al/ASA LDHs.

440

441 **3.6. Antibacterial properties of PBS nanocomposites.** Since packaging includes possibly the
442 contact with food, it is necessary to evaluate the bacteria growth in contact to these materials.
443 The bactericidal activity of synthesized Mg-Al LDHs powders is first examined from tests, using

444 a Gram-positive bacterium, *Staphylococcus aureus* ATCC 6538 (*S. aureus*), and a Gram-
 445 negative, *Escherichia coli* ATCC 8739 (*E. coli*), both common food-borne pathogens (Park,
 446 2015).

447 Secondly, the antibacterial properties of PBS nanocomposites are scrutinized (Table 4). The
 448 results are expressed as percentage of viable cells reduced during test, obtained in respect to
 449 commercial samples (PBS and PuralMg61) which do not show any antibacterial activity and are
 450 used as a reference material.

451
 452 **Table 4.** Antibacterial activity of Mg-Al LDH hybrids and PBS nanocomposite powders,
 453 expressed as the percentage of reduced viable cells

Sample	<i>E. coli</i> ATCC8739 (% inhibition)	<i>S. aureus</i> ATCC 6538 (% inhibition)
PuralMg61	0.0 ± 0.0	0.0 ± 0.0
Mg ₂ Al/HPP	59.0 ± 3.0	75.0 ± 0.0
Mg ₂ Al/ASA	100.0 ± 0.0	100.0 ± 0.0
Mg ₂ Al/TYR	100.0 ± 0.0	100.0 ± 0.0
Mg ₂ Al/TRP	100.0 ± 0.0	100.0 ± 0.0
PBS pure	0.0 ± 0.0	0.0 ± 0.0
PBS-5%Mg ₂ Al/HPP	89.0 ± 4.0	94.0 ± 1.3
PBS-10%Mg ₂ Al/HPP	100.0 ± 0.0	98.0 ± 0.1
PBS-2.5%Mg ₂ Al/ASA	92.0 ± 1.9	100.0 ± 0.0

PBS-5%Mg ₂ Al/ASA	95.0 ± 1.5	100.0 ± 0.0
PBS-10%Mg ₂ Al/ASA	100.0 ± 0.0	100.0 ± 0.0
PBS-2.5%Mg ₂ Al/TYR	57.0 ± 2.6	14.3 ± 9.0
PBS-5%Mg ₂ Al/TYR	99.0 ± 0.0	15.0 ± 10.0
PBS-10%Mg ₂ Al/TYR	100.0 ± 0.0	71.0 ± 10.0
PBS-2.5%Mg ₂ Al/TRP	56.9 ± 2.7	0.0 ± 0.0
PBS-5%Mg ₂ Al/TRP	74.4 ± 7.1	23.6 ± 0.0
PBS-10%Mg ₂ Al/TRP	100.0 ± 0.0	53.5 ± 0.0
PBS-10%Mg ₂ Al/HPP:ASA	100.0 ± 0.0	99.6 ± 0.0
PBS-10%Mg ₂ Al/HPP:TYR	96.8 ± 0.4	10.0 ± 1.7
PBS-10%Mg ₂ Al/HPP:TRP	97.0 ± 0.0	12.0 ± 2.9

454

455 All tested Mg-Al LDH hybrid powders show strong antibacterial activity, and in the case of
456 ASA, TYR and TRP, the cell mortality rate is 100% for both: *E. coli* and *S. aureus*. Only
457 Mg₂Al/HPP LDH shows less activity and the inhibition reaches 59 and 75%, respectively.
458 Although all molecules show a similar bactericidal effect, the mechanism of action is different.
459 TRP is known to have a distinct preference for the interfacial region of lipid bilayers and
460 participates in cation- π interactions, due to significant quadrupole moment formed by the
461 extensive π -electron system of the aromatic indole sidechain (Chan et al., 2006). In the case of
462 ascorbic acid (like other antioxidants), the antimicrobial and antiviral activity may be caused by
463 free radicals which are formed during autoxidation mechanism (Salo et al., 1978), while 3-(4-

464 hydroxyphenyl)propionic acid (HPP) has this activity thanks to presence of the *p*-hydroxyl group
465 on the benzyl ring (Sun et al., 2016).

466 When LDHs are dispersed in PBS matrix, an activity is maintained, however, in most of the
467 cases, it is quantity-dependent. The best results are obtained for PBS composites with
468 Mg₂Al/ASA. Its efficiency in inhibiting *E. coli* increases from 92 to 100% for loading 2.5–10 wt.
469 % and the activity against *S. aureus* is 100% for all composites. The more significant impact of
470 the LDH amount is for Mg₂Al/TYR and Mg₂Al/TRP. Indeed, composites with 2.5 wt. % LDH,
471 the antibacterial activity against *E. coli* is similar (about 57% of inhibition), while against *S.*
472 *aureus*, the 14.3% (for Mg₂Al/TYR) and zero activity (0% of inhibition for Mg₂Al/TRP) is
473 observed. The growth of *E. coli* is completely stopped, with 5 wt. % of Mg₂Al/TYR or 10 wt. %
474 of Mg₂Al/TRP. *S. aureus* seems to be more resistant and for the composites with 10 wt. % of
475 amino acid modified LDHs, the inhibition is of 71 and 53.5%, respectively. Interesting results
476 are obtained for composites with Mg₂Al/HPP: in spite of the fact that the hybrid LDH is showing
477 the worse activity in the series against both bacteria, when it is incorporated into PBS, the
478 inhibition increases up to about 100% efficiency with 10 wt. % of LDH loading.

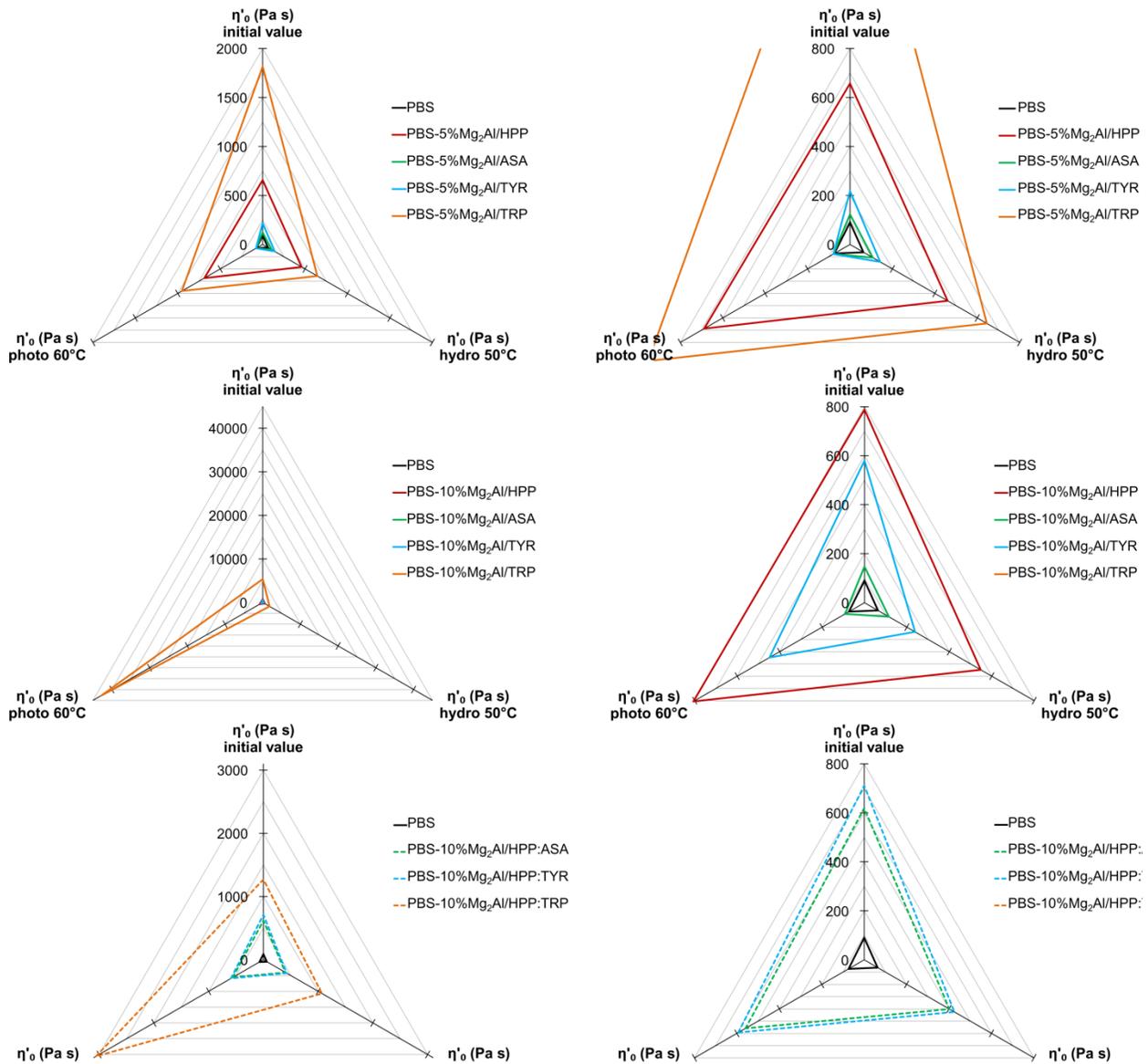
479 Concerning PBS composites with LDH mixtures, around 100% in antibacterial activity against
480 both bacteria is achieved only in the case of PBS-10%Mg₂Al/HPP:ASA. The two other HPP
481 mixtures (with TYR or TRP) are not so efficient. Indeed, in the case of *E. coli*, a synergic effect
482 is however observed as an inhibition higher than for each LDH composition is reached, while the
483 activity against *S. aureus* is much lower and down to about 10% of efficiency. Most probably,
484 some chemical interactions between HPP and amino acids proceed and the mechanism of
485 interaction with bacteria is then disturbed. Indeed, it is possible that the amino groups react with
486 the hydroxyl group of HPP in the confined space, this is illustrated in phenol type molecules

487 reacting with amino acid and proteins (Bittner, 2006). Further tests are required to confirm this
488 hypothesis.

489

490 **3.7. The multi-functionality correlation of PBS composites.** All previously described results
491 have been correlated together and presented in the triangle form in **Fig. 9**. The top corner
492 presents the value of Newtonian viscosity η'_0 of started materials, the left corner represents η'_0
493 after 80 h of photo-ageing and in the right corner η'_0 after 80 h of hydrolysis at 50 °C,
494 respectively. It can be easily noticed, that Mg₂Al/HPP LDH is the best compromise as UV
495 stabilizer to preserve PBS against UV degradation. The effectivity of Mg-Al LDHs with ASA
496 and TYR are worse, and in the case of TRP, a strong crosslinking effect not suitable for polymer
497 processing is observed when it is used in higher amount. On the other hand, Mg₂Al/ASA LDH
498 can be used as an additive with HPP for reducing the rate of hydrolysis as well as the bacteria
499 activity.

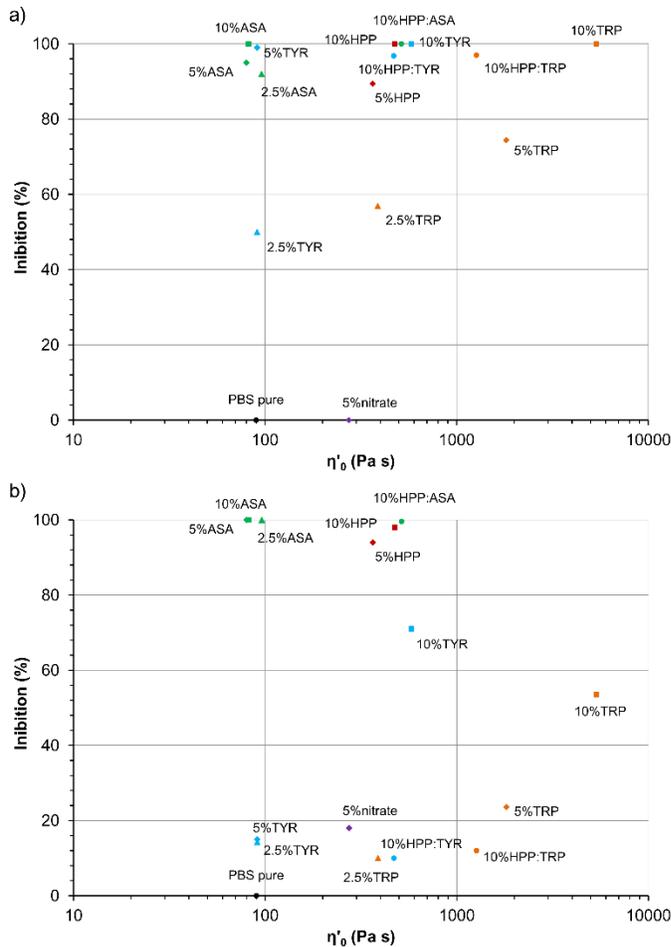
500



501
 502 **Fig. 9.** Radar-type correlation between the Newtonian viscosities η'_{0} before and after 80 h in
 503 photo-ageing and hydrolysis conditions for PBS and PBS-Mg-Al LDH composites; overall view
 504 (right) and zoom region (left).

505
 506 **Fig. 10** displays the correlation of Mg-Al organo-modified LDH between its antibacterial
 507 activity and the chain extension effect. All composites with Mg₂Al/ASA and composites with
 508 Mg₂Al/HPP or Mg₂Al/TYR LDHs in amount of 5 wt. % (or more) show over 90% inhibition

509 against *E. coli* bacteria growth (**Fig. 10a**). Mg₂Al/TRP LDH filler may have similar effectiveness
 510 if it used in higher amount or in combination with Mg₂Al/HPP. In the case of Gram-positive
 511 bacterium like *S. aureus*, the composites with Mg₂Al/ASA and Mg₂Al/HPP LDH are the only
 512 compositions efficient, as well as the mixture of the two (**Fig. 10b**).
 513



514
 515 **Fig. 10.** The correlation of antibacterial effect, expressed as inhibition (%) of bacterial growth
 516 against (a) *E. coli* and (b) *S. aureus*, related to the Newtonian viscosity η'_0 (Pa.s).

517
 518 Although the high antibacterial activity, especially against *E.coli*, can be obtained for these
 519 composites, they significantly differ in chain extender effect. The values of Newtonian viscosity

520 is about 100 Pa.s for ASA and TYR (5 wt. %), 600–800 Pa.s for composites with HPP and its
521 mixtures with ASA and TYR, finally over 1000 Pa.s for composites with Mg₂Al/TRP LDH.
522 Thus, the choice of LDH filler should also be determined as a function of the application and its
523 associated required properties.

524 3.8. Scale-up: toward applicative possibilities

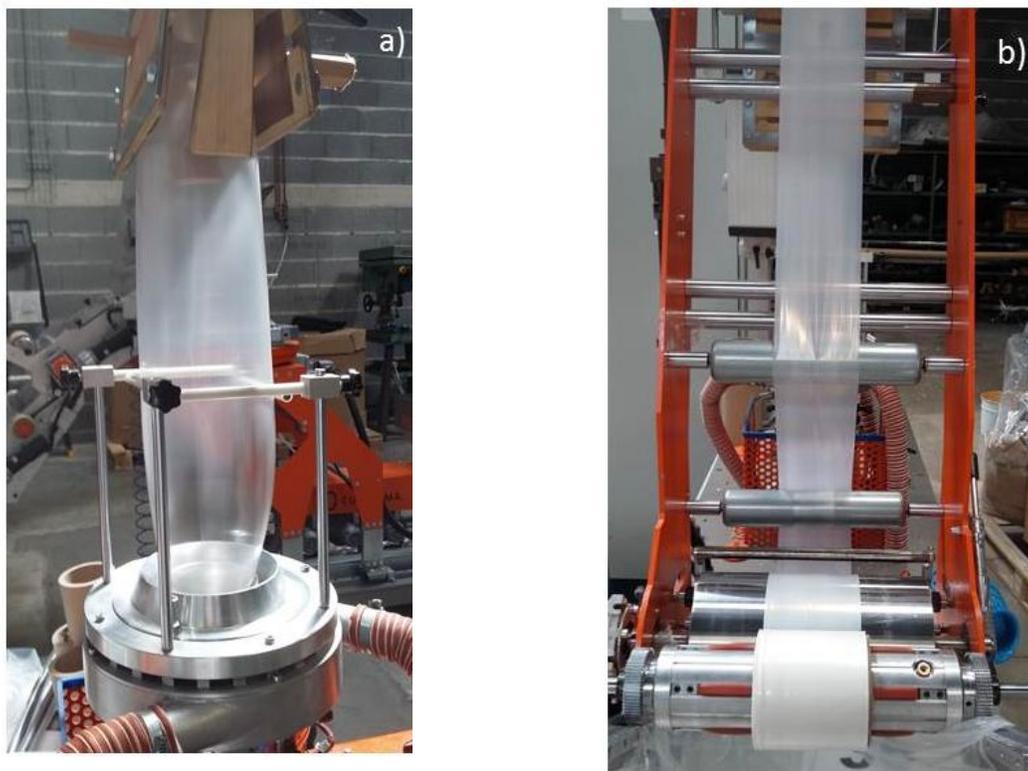
525 The filler Mg₂Al/HPP is evaluated in PBS in a scale-up process. From the thin films obtained
526 in a larger quantity (process of \approx 10 kg/h of PBS composites), it is then possible to rationalize the
527 possible applicability. This aspect of our study is unusual, since such consideration is scarcely
528 reported in the literature for polymer composite domain. The thin film PBS-Mg₂Al/HPP presents
529 a good appearance at the extruder outlet (**Fig. 11**) with a haze color as for PBS itself after
530 extrusion process. The composite film exhibits an increase in modulus, maximum at strain,
531 extension as well as enhanced tearing properties compared to PBS itself (**Table 5**). Indeed, an
532 interesting aspect is the tearing properties that is superior (of 25%) in both longitudinal and
533 transversal direction compared to PBS. This is one of the key parameter for its use as thin films
534 for packaging. However, the WVTR remains constant, indicating that even if some mechanical
535 properties are met, the barrier properties remain to be solved.

536 **Table 5.** Mechanical properties and WVTR of thin film of PBS and PBS Mg₂Al/HPP composite

	PBS	PBS composite
Film thickness (μm)	25	35
Modulus (MPa)	410	650
Max at strain (MPa)	35	41
Extension (mm)	2.9	6.1
Tear (N/mm)		

Longitudinal	505	610
Transversal	585	780
WVTR (g/m ² /day)	480 ± 4	377 ± 4

537



538 **Fig. 11.** Photographies of the PBS-Mg₂Al/HPP composite at a) the output of the fan extruder,
539 and b) the exit of roll.

540

541 CONCLUSION

542 As usual LDH appears in this study as an adaptive toolbox in combination with interleaved
543 organic molecules of interest for desired application. The combination of two LDH filler
544 associating anions HPP and ASA appears as an efficient compromise to perform against photo-

545 aging and hydrolysis of PBS, as well as cancelling the bacteria activity, this by keeping an
546 improved chain extension effect, superior to LDH-HPP itself. It is worth to mention that ASA
547 molecules is known to suffer from temperature and light, it appears to be less sensitive and
548 protected when ensconced into LDH gap.

549 A technological scale-up to produce larger amount of PBS composite than in the laboratory
550 frame is possible. The obtained thin film is found to be more resistant to extension and tearing,
551 that is highly suitable for flexible packaging, and keeping most of the properties of the PBS
552 intact. Evidently, one of the drawbacks is the high WVTR that needs to be strongly diminished
553 compared to PBS free of filler, thus weakening for now a possible direct applicability, but
554 keeping open the cases where the barrier to water is not the main requirement.

555

556 **ASSOCIATED CONTENT**

557 **Supporting Information**

558 The Supporting Information includes: TGA and DTGA traces of obtained PBS
559 nanocomposites, XRD patterns of PBS nanocomposites with 10 wt. % of Mg-Al organo-
560 modified LDHs, UV-vis transmittance and fluorescence spectra of PBS and PBS composites
561 with 5 wt. % of Mg-Al organo-modified LDHs during photo-degradation at 60 °C, evolution of
562 Newtonian zero-shear viscosity η'_0 and succinic acid concentration during hydrolysis of PBS and
563 PBS-Mg-Al LDH composites at 50 °C.

564

565 **Author Contributions**

566 F.L. and V.V. conceived the project. A.A.M. prepared the samples and performed UV-ageing
567 and hydrolysis experiments. G.T., L.S. and A.C. were responsible for DSC and TGA analysis,
568 while A.A.M. carried out the rheology, UV-vis, SEM, XRD and fluorescence measurements.
569 N.B.C. and D.G determined antibacterial properties. A.A.M and F.L. analyzed the data and
570 prepared the manuscript. All authors contributed to the discussion of the results. All authors have
571 given approval to the final version of the manuscript.

572

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580 respectively.

581

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