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27 **ABSTRACT**

28 To investigate the influence of chemical compositions of organoclays on the thermal stability and fire
29 behavior of PLA nanocomposites, 2, 6 and 8 wt% of single and hybrid Brazilian organically-modified
30 montmorillonites (OMt), containing ammonium and phosphonium based surfactant - di-(hydrogenated
31 tallow) dimethyl ammonium chloride (HTA), trihexyl tetradecyl phosphonium chloride (TDP), di(alkyl
32 ester) dimethyl ammonium chloride (EA) and ethoxylated tallow amine (ETA) - were added to PLA
33 using a melt-compounding process. It was noticed that the addition of OMt and melt-compounding
34 contributed to a decrease of the initial decomposition temperature and average molecular mass of PLA,
35 assessed by thermogravimetric analysis (TGA) and gel permeation chromatography (GPC),
36 respectively. Moreover, PLA nanocomposites with single OMt (TDP and HTA) showed lower thermal
37 stability than those with hybrid OMt. PLA nanocomposites with hybrid OMt containing EA and ETA
38 displayed higher fire-reaction performance under cone calorimeter test. Comparing with neat PLA,
39 these nanocomposites registered a peak heat release rate (pHRR) reduction of 29% and 38%, and a fire
40 index grow rate (FIGRA) reduction of 32% and 37%, respectively, as well as the absence of melt
41 dripping during combustion. The enhancement of the fire-reaction behavior was related to the
42 nanoparticles high degree of dispersion and compatibility between PLA and nanoparticles,
43 characterized in a previous work (Alves et al., 2019), which contributed to the formation of an effective
44 protective layer on the condensed phase during combustion.

45

46 Keywords: Organoclay; Poly (lactic acid); Polymer nanocomposite; Thermal stability; Fire
47 performance; Cone calorimeter.

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52 **1. Introduction**

53 Nowadays, there is global concern about sustainability and environmental impacts associated
54 with the production, consumption and disposal of petroleum-based polymer materials. This has been
55 causing an increase in the demand for new environment friendly materials such as the biodegradable
56 biopolymers derived from natural sources. Poly (lactic acid) (PLA) is one of the most promising
57 alternatives to more conventional plastics (Chow et al., 2018; Tawiah et al., 2018). PLA is a linear
58 aliphatic polyester, considered as a biopolymer because of its biodegradability under composting
59 conditions, biocompatibility, totally derived from renewable sources (Garlotta, 2001; Ahmed and
60 Varshney, 2011; Armentano et al., 2013).

61 The studies correlated to PLA properties have been gaining strength in order to expand its
62 industrial applications. Currently, new industrial applications for PLA have been reported, such as in
63 the production of films and food packaging, fibers for the textile industry, materials for the automobile
64 industry, electrical and electronic applications, agricultural, furnishing, construction, among others
65 (Ahmed and Varshney, 2011; Armentano et al., 2013; Castro-Aguirre et al., 2016; Chow et al., 2018).

66 In summary, although PLA has the potential to increase its applicability, it still shows limitations
67 for example, low thermal resistance, brittleness, low ductility and toughness, low crystallization rates,
68 ease of ignitability and high flammability (Sinha Ray et al., 2003; Murariu and Dubois, 2016; Chow et
69 al., 2018).

70 Many works have been made to obtain hybrid-based PLA with improved properties by mixing
71 with other biodegradable (Gunning et al., 2014; Bouakaz et al., 2017; Adrar et al., 2018) and non-
72 biodegradable plastics (Balakrishnan et al., 2010; Kaczmarek and Vuković-Kwiatkowska, 2012),
73 organic compounds (Chen et al., 2013; Sato et al., 2013) and additives (Gumus et al., 2011), and by
74 dispersion of various nanoparticles to obtain polymer nanocomposites (Almeida et al., 2012; Jung et al.,
75 2014; Bouakaz et al., 2015; Huang et al., 2015; Akkari et al., 2016; Guo et al., 2016). Among the various
76 types of known nanoparticles, organoclays, mainly organically-modified montmorillonites, have been

77 widely considered to prepare PLA nanocomposites (Chang et al., 2002, 2016; Jiang et al., 2007; Darie
78 et al., 2014). Studies aimed to the incorporation of organoclays into PLA should take into account
79 factors such as processing techniques and conditions, amount of reinforcement, and chemical
80 compatibility between phases, governed by the surfactant agents present in the organoclays (Sinha Ray
81 et al., 2002, 2003; Sinha Ray and Okamoto, 2003). PLA and its nanocomposites can be produced and
82 processed using conventional equipment and methods. However, some adaptations are often necessary,
83 due to the susceptibility of PLA to thermally degrade during processing at high temperature, caused by
84 hydrolysis of PLA molecules, especially in the presence of water and impurities (Fambri and Migliaresi,
85 2010; Nishida, 2010; Marras and Zuburtikudis, 2012; Araujo et al., 2014).

86 One of the major concerns regarding the applicability of PLA in several sectors such as
87 electronic equipment, automobile and civil construction sector, is correlated with its high flammability.
88 PLA is considered a flammable material with low fire performance without the addition of flame
89 retardants (FR), demonstrating easy ignition and flame dripping (Chow et al., 2018). Basically, these
90 properties are correlated with the intrinsic properties (i.e. molecular structure and chemical
91 composition) of the polymeric material, and can be enhanced by chemical modification and/or
92 incorporation of flame retardants (Chow et al., 2018; Tawiah et al., 2018).

93 It has been shown that improvements in the fire performance of PLA can be achieved by the
94 addition of phosphorus and hypophosphite-based flame retardants (IR) (Song et al., 2011; Ye et al.,
95 2016); intumescent flame retardant (IFR) (Réti et al., 2008; Ke et al., 2010; Kang et al., 2019);
96 nanofillers (Liu et al., 2015; Jiang et al., 2019); and also by chemical modification (Yu et al., 2018).
97 However, in order to develop significant flame resistance properties, conventional flame retardants must
98 be incorporated into the PLA in high amounts (20-40 w%) (Chow et al., 2018).

99 Nanofillers, such as organoclays (Laoutid et al., 2006; Rahatekar et al., 2010; Jiang et al., 2019),
100 carbon nanotubes (Kashiwagi et al., 2005; Cipiriano et al., 2007; Rahatekar et al., 2010) among others,
101 are being used as potential flame retardant for several polymers. Some studies have reported that
102 organically-modified montmorillonites can act as good FRs (Zhang and Wang, 2018), including for

103 PLA (Wei et al., 2013; Liu et al., 2015), as nanoparticles contribute to the development of a thermal
104 insulation layer on the surface of the burning material during combustion, acting as a barrier to the
105 transport of mass and energy between the flame and the material surface, reducing the heat release rate
106 (HRR) and dripping. These effects depend on the amount, degree of dispersion and interaction of the
107 nanoparticles in the PLA, which are strongly correlated with the surface modification of the material.
108 Although this type of material presents good characteristics as FR, they are still not enough to produce
109 flame-retarded PLA with fire safety regulatory requirements (Chow et al., 2018).

110 The benefits of a well dispersed organically-modified montmorillonite to the properties of PLA
111 have been published, showing enhancement of the storage modulus and initial temperature of thermal
112 degradation, besides decreases of the peak of heat release rate (pHRR) (Liu et al., 2015). PLA
113 nanocomposites have been shown to burn differently when compared with neat PLA, as the organoclay
114 reduces PLA combustion rate (Wei et al., 2013).

115 The improvement of fire performance usually requires the incorporation of high amounts of
116 FRs, which often decreases the material mechanical properties due to incompatibility between the
117 phases of the system. The development of hybrid FR composed of an inorganic material modified with
118 organic compounds with compatibility with PLA, as for example an organoclay (Jiang et al., 2019),
119 has been seen as a good strategy to simultaneously increase the mechanical, thermal and fire
120 performance of PLA.

121 Another promising approach in this field is the combination of FR, aiming to achieve synergistic
122 effects in terms of the fire performance of the material, as well as reduce global FR concentration (Ke
123 et al., 2010; Kang et al., 2019). In this sense, ternary systems that aim at OMt synergism with traditional
124 flame retardants have been gaining attention (Murariu et al., 2010; Cheng et al., 2012). The main interest
125 of these combinations is to achieve optimum PLA combustion performance (i.e. self-extinguishable,
126 smoke suppression, improved dripping behavior) according to safety requirements without diminishing
127 mechanical and thermal properties, which is generally associated with degradation of the polyester
128 matrix at high FR loading (Song et al., 2011; Ye et al., 2016).

129 Researches have been made to obtain new organoclays with high performance for clay polymer
130 nanocomposites (CPN), using different chemical compounds and preparation methods, for instance
131 using a mixture of surfactants (Guégan, 2010, 2013; Zhang et al., 2013; Zhuang et al., 2015; Alves et
132 al., 2016, 2017, 2018; Liao et al., 2016). Cationic surfactants based on quaternary ammonium salts
133 generally have good compatibility with a great number of polymers, but have low thermal stability (Ha
134 and Xanthos, 2009; Sarkar et al., 2011, 2012; Alves et al., 2016, 2017), whereas phosphonium-based
135 surfactants (Ha and Xanthos, 2009; Freitas, 2010; Alves et al., 2016) and non-ionic surfactants based
136 on ethoxylated amines (Shen, 2001; Silva et al., 2012, 2014; Alves et al., 2017) confer high thermal
137 resistance to organoclays. Hybrid organic montmorillonite (HOMt) with combined properties such as
138 compatibility and thermal stability was reported in previous works (Alves et al., 2018, 2019). The
139 influence of different organoclays on the morphology of PLA nanocomposites has been reported and
140 shown to depend on the compatibility between the organic compounds and PLA.

141 In this present work, PLA/OMt nanocomposites were investigated based on the assumption that
142 the combination of modifying organic compounds with different chemical composition, such as
143 phosphonium-based, which has high thermal resistance and potential flame retardancy by the
144 phosphorus component, with di(alkyl ester) dimethyl ammonium chloride (EA) and ethoxylated tallow
145 amine (ETA), with potential compatibility with PLA, can result in a material with improved thermal
146 and fire resistance.

147

148 **2. Materials and Methods**

149 *2.1. Materials*

150 PLA (grade 3052D) supplied by NatureWorks LLC with a D-lactide content around 4% was
151 used in this work. Organically-modified montmorillonites produced in a previous work containing
152 single and dual organic compound based on ammonium and phosphonium salt - di-(hydrogenated
153 tallow) dimethyl ammonium chloride (HTA), trihexyl tetradecyl phosphonium chloride (TDP), di(alkyl

154 ester) dimethyl ammonium chloride (EA) and ethoxylated tallow amine (ETA) (Alves et al., 2016, 2017,
155 2018), and two commercial organoclays, Cloisite 20A and Cloisite 30B, supplied by Southern Clay
156 Products, aim to compare with the other organoclays, were used to prepare PLA nanocomposites.

157 *2.2. Samples preparation*

158 The PLA nanocomposites containing 2 wt%, 6 wt% and 8 wt% of organoclay were produced
159 using first a counter-rotating internal mixer (Brabender Plasti-Corder[®] W50EHT) to prepare
160 masterbatches with 20 wt% of organoclay, and secondly a co-rotating twin screw extruder (Collin
161 Kneuter 25X36D), with diameter of 25 mm and L/D of 36 to dilute the materials in the desired
162 composition, following the method described in a previous work (Alves et al., 2019). The PLA was
163 extruded at the same conditions labeled as EPLA. **Table 1** summarizes all sample code of the PLA
164 nanocomposites with their respective organoclay types, chemical composition and amounts.

165

166 **Table 1.** Composition of PLA nanocomposites.

167

168 *2.3. Characterization procedure*

169 In order to evaluate the samples thermal stability, thermogravimetric analysis (TGA) was
170 performed on a Mettler Toledo DSC 1 Star System equipment under nitrogen flow of 30 ml/min, heating
171 rate of 10 °C/min from 30 to 700 °C, with approximately 10 mg of sample in alumina crucibles. The
172 actual amount of surfactants on the organoclays were determined by Dweck's method (Dweck et al.,
173 2011). The initial temperature of thermal degradation was determined at a 5 wt% of mass loss ($T_{5wt\%}$).

174 Also, the molecular mass of processed PLA and some selected PLA nanocomposites were
175 determined by gel permeation chromatography (GPC) (LC-VP, Shimadzu Co.), to verify the possible
176 degradation occurred during processing. Polystyrene standards were used for calibration and
177 tetrahydrofuran (THF) as solvent. The samples were injected at a concentration of 4.0 mg/ml with a
178 flow rate of 1.0 ml/min at 45 °C.

179 Cone calorimeter experiments were performed to investigate the effects of organoclays on the
180 fire behavior of PLA nanocomposites. The tests were conducted on a cone calorimeter, BECC model
181 equipment according to ISO 5660-1 (International Organization for Standardization, 2015). For each
182 material, three circular-shaped specimens with a thickness of 3 mm and a diameter of 75 mm were
183 exposed to a constant heat flux of 25 kW/m². Fire reaction parameters such as the time to ignition (TTI),
184 which is the time required for the irradiated sample to develop a sustainable flame; the peak heat release
185 rate (pHRR), defined as the maximum value of heat release rate (HRR); the total heat evolved (THE),
186 which is the integral of the HRR vs time curves determined between TTI and flameout time; and the fire
187 growth rate index (FIGRA), defined as the maximum quotient of HRR(t)/t, were evaluated in the present
188 work.

189

190 3. Results and discussion

191 3.1. Thermal stability

192 Characteristic mass loss (TG) and derivative mass loss (DTG) curves are shown in **Figure 1** for
193 EPLA and PLA nanocomposites with 6 wt% of OMt, and the thermal parameters of EPLA and all
194 nanocomposites samples can be seen in **Table 2**. The organoclays, with the exception of C20A,
195 decreased the initial degradation temperature of PLA (T_{5%}, in **Table 2**) and this effect increased with
196 OMt content, as the same trend was already reported with different types of organoclays, including
197 Cloisite 30B (Chang et al., 2002; Mclauchlin and Thomas, 2009; Molinaro et al., 2013).

198

199 **Figure 1.** (a) TG and (b) DTG curves of EPLA and CPN with 6 wt% OMt.

200

201 The phosphonium surfactant in MTDP, which leads to the most stable OMt among the
202 nanofillers used, according to previous works (Alves et al., 2016, 2017, 2018), caused the greatest
203 reduction in the initial temperature of thermal degradation of PLA after melt mixing, followed by

204 MHTA. The PLA nanocomposites containing hybrid OMT, mainly EA and ETA with phosphonium salt
205 in its composition, presented higher $T_{5\%}$ than MTDP. This result suggests that the TDP surfactant could
206 be promoting an earlier thermal degradation of PLA and that the addition of the second surfactant could
207 be reducing this effect.

208

209 **Table 2.** Thermogravimetric analysis parameters determined from TGA and DTG curves for EPLA and
210 PLA nanocomposites.

211

212 The reduction on the initial degradation temperature of PLA nanocomposites could be associated
213 to molecular scission during melt mixing with OMT, induced by the shearing forces. It is known that
214 PLA is susceptible to hydrolysis process, depending on process conditions, presence of water and
215 impurities (Pluta, 2006; Nishida, 2010). GPC measurements were carried out in representative samples
216 to ascertain if the lowering of $T_{5\%}$ could be associated to PLA chain scission. Results are presented in
217 **Table 3.** The values of the number-averaged molecular mass, \bar{M}_n (103 kDa) and weight-averaged
218 molecular mass, \bar{M}_w (199 kDa) of extruded PLA drastically decreased with the addition of 6 wt% of
219 OMT. Comparing \bar{M}_n values of CPN samples with their respective $T_{5\%}$, it is possible to see that $T_{5\%}$
220 reduction resulted proportional to the reduction of \bar{M}_n . The highest decrease was caused by the thermal
221 process with MTDP (59 kDa), probably due to some catalytic effects caused by TDP surfactant that
222 accelerated the degradation of PLA chains by hydrolysis, and the lowest one by C20A (84 kDa), which
223 matches well and justifies the TGA results.

224

225 **Table 3.** Molecular mass data of EPLA and CPN samples with 6 wt% of OMT.

226

227 Comparing CPN materials containing C20A and MHTA, both of them being OMt modified with
228 the same surfactant but different pristine montmorillonite, results also show differences, as PN6MHTA
229 nanocomposite presented lower \bar{M}_n value and lower thermal stability than PN6C20A. The results
230 suggest that either organic and inorganic phase composition contributed to reduce the thermal stability
231 of PLA during melting, probably due to hydrolysis caused by traces of water and impurities in the clay
232 mineral, catalytic effect of free hydroxyl group on the montmorillonite layers and/or aminolysis
233 associated with ammonium surfactant (Nishida, 2010; Kontou et al., 2012). Finally, changes in the melt
234 rheology, i.e., increased viscosity caused by the presence of the organoclay, could also play a role on
235 the degradation of PLA.

236

237 *3.2. Fire behavior*

238 The cone calorimeter, based on the oxygen consumption principle, is an effective and usual
239 technique to investigate the combustion behavior of materials. Representative curves of the heat release
240 rate as a function of time for EPLA and PLA nanocomposites with 8 wt% of OMt are shown in **Figure**
241 **2**, and the variation of the fire reaction parameters as function of OMt type and content are recorded in
242 **Figures 3 and 4**.

243

244 **Figure 2.** Heat release rate curves of EPLA and PLA nanocomposites with 8 wt% of OMt.

245

246 Analyzing the shape of the curves in **Figure 2**, all the samples, except the unfilled EPLA,
247 generally presented a shoulder at the beginning of the curve (around 60-80 s). This behavior is typically
248 associated with the formation of a thermal insulator layer on the burning surface of the material. This
249 insulator layer consists of a combination of the accumulation of layered inorganic clay mineral stacks,
250 carbonaceous residue and charred polymer. This layer acts as a protective thermal barrier reducing peak
251 heat release rate and can be an indicative of char enhancement and flame retardancy. It is known that

252 the effectiveness of the inorganic nanofillers layers to retard the combustion of the polymer depends on
253 the capacity of the barrier properties between the condensed phase and the flame, inhibiting the
254 flammable volatiles and the heat transport between flame and polymer (Wei et al., 2013; Ahmed et al.,
255 2018).

256 As expected, EPLA was highly flammable, causing the flame ignition of the cotton on the
257 specimen support due to melted polymer drips. This effect can be observed by the prolongation of EPLA
258 curve after 200 s. These melt drips were visually extinguished by the addition of 2 wt% of most of OMt,
259 except PN2MTDP, PN2MHTA and PN2HMPHTA. When OMt content in these samples was increased
260 to 6 and 8 wt%, the intensity of the flame was reduced, and melt drips were totally extinguished, owing
261 to an increase of the shield effect of the insulator layer. For the CPN series with HMPEA, HMPETA,
262 C20A and C30B, this melt dripping behavior was not observed, even with 2 wt% of nanofiller. The
263 insulator barrier formation and its efficiency generally depends on clay mineral dispersion, content and
264 interaction with the matrix, and thermal stability of clay modifier (Wei et al., 2013; Shabaniyan et al.,
265 2016). This suggested that these OMts promoted an efficient barrier effect, due to the good dispersion
266 and interaction of these organoclays in the PLA, as observed in previous work (Alves et al., 2019).
267 Additionally, it is known that an increase of viscosity conferred by the incorporation of nanoparticles,
268 as organoclays, can have a positive effect on flame retardancy of polymeric material by modifying the
269 physical burning process and/or the chemistry in the condensed phase, in particular by slowing down
270 the emission of combustible volatiles and avoiding polymer dripping and by mechanically stabilizing
271 the charred structures (Lopez-Cuesta, 2012; Ahmed et al., 2018).

272 The total heat evolved (THE) is presented in **Figure 3** for all nanocomposites. It was observed
273 that the THE parameter of EPLA remained almost unaltered after OMt loading in all CPN series. This
274 indicates that the insulator layer containing organoclays probably behaved as a protective physical
275 barrier, reducing HRR, but without contributing to the lowering of the total heat involved in the
276 combustion, as was also noted by Wei et al. (2013).

277

278 **Figure 3.** Evaluation of the total heat evolved (THE) and peak heat release rate (pHRR) with organoclay
279 type and content.

280

281 A drawback noticed in this work was the reduction of the time to ignition (TTI) for all dispersed
282 layered fillers and content, as can be see in **Figure 4**. This behavior was related to nanofillers-catalysed
283 oxidation of the gases generated at the surface of the condensed phase by thermal volatilization of the
284 PLA matrix (Wei et al., 2013). It can be supposed that the early ignition on the nanocomposite materials
285 could also be associated with organoclay surfactants and/or small PLA molecules produced by thermal
286 degradation, as indicated by TGA and GPC analyzes, which are species more thermally unstable and
287 flammable, and therefore more volatile and susceptible to early combustion.

288

289 **Figure 4.** Evaluation of the time to ignition (TTI) and fire index growth rate index (FIGRA) with
290 organoclay type and content.

291

292 The results show that the formation of the insulator layer depended on OMt chemical
293 composition and OMt content, directly influencing the combustion behavior of the materials. Some
294 representative digital photographs of cone calorimeter residues are shown in **Figure 5** and the amount
295 of final residue in **Figure 6**, aiming to a better understanding of nanofillers' effects on the combustion
296 behavior of the materials. It is possible to observe that the amount and morphology of the char/inorganic
297 residues became larger and more compact with increasing clay content, leading to a gradual reduction
298 of pHRR (**Figure 3**). EPLA presented no cone residue, as can be seen in **Figure 6**, and a pHRR of 800
299 kW/m². In addition, all nanocomposites with 2 wt% of OMt presented a small amount of residue and
300 nearly no effect on pHRR. CPN with 6 and 8 wt% of MTDP presented lower combustion residue content
301 with a great number of large cracks on the char surface. These cracks reduced the barrier effect, allowing
302 the propagation of the flame to the material at the bottom and the degradation of combustible volatiles,

303 leading to almost no reduction in pHRR (Wei et al., 2013). In contrast, increasing the amount of HOMt
304 – HMPEA and HMPETA, and C30B, led to a larger and more compacted char/inorganic insulator layer
305 with a reduced number and size of cracks (**Figures 5 and 6**). As a result, an effective thermal barrier
306 was created, resulting on a great decrease of pHRR to 570 kW/m², 500 kW/m² and 460 kW/m²,
307 respectively for nanocomposites with 8 wt% of MPETA, MPEA and C30B. This represents an
308 important reduction of 29, 38 and 43% in the pHRR value in relation to EPLA. This fact may be once
309 again correlated with a higher dispersion degree and interaction of the inorganic fillers with the matrix,
310 owing to its good compatibility with PLA (Alves et al., 2019), which also probably had higher catalytic
311 effect to hold the polymer char, leading to the formation of a more compact and effective insulator layer.

312 The fire growth rate index (FIGRA) is an important parameter required for regulatory purposes,
313 which can estimate the size of the fire as well as fire spread (Haurie et al., 2013; Ahmed et al., 2018).
314 The FIGRA values of the samples are shown in **Figure 4**. Generally, this parameter follows the same
315 trend of the pHRR. It can be observed that the FIGRA was reduced by the increment of OMt content.
316 PLA nanocomposites containing MTDP displayed the higher FIGRA values, even than EPLA,
317 confirming the poor fire performance of these materials, which was related to the incompatibility
318 between phases. On the other hand, the materials containing 8 wt% of HOMt, MPEA and MPETA, and
319 commercial organoclay C30B, showed a remarkable reduction in the FIGRA value of 32, 37 and 39%,
320 respectively, when compared with EPLA.

321

322 **Figure 5.** Digital photographs of CPN nanocomposites residues obtained from cone calorimeter test.

323

324 The presented results suggest a better improvement on flame performance of PLA
325 nanocomposites by intercalation of the hybrid OMt containing trihexyl tetradecyl phosphonium chloride
326 (TDP) with ethoxylated tallow amine (ETA) and di(alkyl ester) dimethyl ammonium chloride (EA)
327 surfactants, and Cloisite 30B containing methyl tallow bis-2-hydroxyethyl quaternary ammonium

328 surfactant (MT2EtOH) than the single OMT containing only TDP or di-(hydrogenated tallow) dimethyl
329 ammonium chloride (HTA). It is possible that the organoclays containing ETA, EA and MT2EtOH
330 surfactants can strongly interact with either PLA chains and the chain radicals and/or volatiles formed
331 during the burning process. In fact, ETA and MT2EtOH contain hydroxyl groups that can hydrogen-
332 bond with the carboxyl groups of PLA, and EA contain ester groups. Mofokeng et al. (2016) proposed
333 a thermal degradation mechanism for Cloisite 30B and Cloisite 15A (contain the same surfactant than
334 MHTA and C20A organoclay) filled PLA nanocomposites. The authors confirmed that -OH groups on
335 Cloisite 30B surfactant strongly interact with the free radicals of PLA chains and the volatile
336 degradation products such as CO, CO₂, acetaldehyde and some of the cyclic oligomers, resulting in an
337 immobilization effect, which delays the volatilization of these products and the degradation process.

338

339 **Figure 6.** Amount of residue for EPLA and PLA nanocomposites.

340

341 Therefore, the enhancement observed in those materials is probably associated to the better
342 compatibility and interaction between these organoclays and PLA associated with the functional groups
343 presented in the organic compound, which provided some reaction of active hydroxyl-carboxyl groups
344 between organoclay and PLA during combustion, trapping free radicals and volatiles in the gas phase
345 and promoting char formation in the condensed phase and an effective protective barrier enhancement,
346 protecting the matrix during combustion. On the other hand, this trend was not observed in PLA
347 nanocomposites with MHTA and MTDP, probably due to the lack of functional groups in surfactants
348 present in these organoclays.

349

350 **4. Conclusions**

351 Motivated by a previous work that verified that the morphology and structure of PLA
352 nanocomposites depended on the chemical composition of montmorillonites surfactants, the influence

353 of montmorillonite functionalized by single and dual ammonium and phosphonium compounds on PLA
354 thermal stability and fire performance was investigated.

355 TGA and GPC analyzes revealed that organoclays promote PLA chain scission and molecular
356 mass loss during thermal processing, which reduces the thermal stability of PLA nanocomposites.
357 Despite the high thermal stability of the phosphonium-based compound, clays containing high amounts
358 of this surfactant exhibited lower thermal stability due to its incompatibility with PLA and possibly
359 catalytic effects that caused degradation of PLA chains. This fact affects the fire performance of PLA
360 nanocomposites causing early ignition of the material. On the other hand, the good dispersion of OMt
361 platelets, such as in PLA nanocomposites containing ETA, EA and C30B, where the organic modifiers
362 have good compatibility and interaction with PLA, promoted an effective insulator layer in the burnt
363 surface of the material, preventing mass and heat transfer between the material and the flame, decreasing
364 pHRR, FIGRA and PLA melt dripping.

365 Despite the shortcomings detected in the thermal stability and fire behavior of PLA
366 nanocomposites, hybrid organo-montmorillonites can be a viable alternative as flame retardant. This is
367 a recent and open research field and the future focus is to develop hybrid OMt containing a combination
368 of organic compounds with compatibility, environmentally friendly and flame retardant characteristics,
369 such as ethoxylated amines and phosphorus-based compounds containing polar groups, among others,
370 aiming to produce flame-retarded PLA with enhanced mechanical performance.

371

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377

378

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