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1 **The mixed impact of nanoclays on the apparent diffusion coefficient of additives in**  
2 **biodegradable polymers in contact with food**

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12 **Abstract**

13 In face of growing environmental concerns, biodegradable and bio-sourced plastic  
14 nanocomposites are emerging as a new class of materials, especially for the food packaging  
15 sector. However, their use in food contact raises new issues in term of consumer safety.

16 The aim of this study was to determine the impact of nanoclays on the apparent diffusion  
17 coefficient ( $D_{app}$ ) of selected additives from biopolymers into fatty food simulants. For the most  
18 part, nanoclay addition has a non-conventional impact. To understand this, the following  
19 parameters were studied: (i) the exfoliation state of nanoclay platelets in the polymer matrix,  
20 (ii) the sorption of food simulant by the polymer matrix, and (iii) the crystallinity of the  
21 materials. At first glance, solvent uptake and crystallinity agree with the results of diffusivity,  
22 however these parameters cannot explain the extreme differences between  $D_{app}$  values.

23 Keywords: nanoclays, biopolymer, apparent diffusion coefficient ( $D_{app}$ ), additives, food  
24 packaging

## 25 **1 Introduction**

26 The growing global production and consumption of plastic materials engenders serious  
27 environmental concerns (Kirwan and Strawbridge, 2003), primarily the need to implement eco-  
28 efficient end-of-life treatments. For many years, alternative materials based on bio-sourced and  
29 biodegradable polymers have been considered as innovative and promising materials for future  
30 food packaging applications (Tharanathan, 2003; Sorrentino et al., 2007). However, the  
31 substitution of plastic in all its various uses in food packaging remains difficult given the broad  
32 spectrum of functionality offered by petroleum-based polymers. In addition to their high water  
33 sensitivity, the properties of biodegradable materials make them uncompetitive in comparison  
34 with those of conventional plastic polymers, particularly in terms of barrier properties. The  
35 addition of reinforcing fillers such as clay nanoparticles, giving rise to the formation of a bio-  
36 nanocomposite material, is widely considered as the solution to this problem (Perumal et al.,  
37 2018).

38 The introduction of nanotechnologies to the field of food packaging raises new issues  
39 related to consumer safety. Research has focused on the exposure of consumers to nanoparticles  
40 through contamination of the food in contact with nanocomposite materials. There is a  
41 consensus in the research on the migration of nanoclay that its limited diffusion under a  
42 nanoform in a polymeric matrix prevents its migration into food (Šimon et al., 2008). Like any  
43 material in contact with food, nano- and bio-nanocomposite materials are subject to the  
44 European framework regulation UE 1935/2004. In the absence of specific regulations covering  
45 their use in contact with food, the suitability for food contact applications of nanocomposite  
46 packaging are assessed according to the recommendations established for plastic materials  
47 specified in the regulation EU/10/2011.

48 Given the impact of nanoclays on the transfer properties of materials (Muñoz-Shugulí et  
49 al., 2019), it is logical to investigate their impact on the migration of property-enhancing

50 plastics additives such as plasticizers, UV-stabilizers, anti-oxidants, and anti-static agents  
51 (Figge, 1980). The impact of nanoparticles on the potential migration of low molar mass  
52 additives has received little attention, the only studies having focused on plastic-based  
53 nanocomposite materials. These studies, performed on nanocomposite materials, specifically:  
54 PETs (Farhoodi et al., 2016), polyamides (Pereira de Abreu et al., 2010), and polyolefins  
55 (Otero-Pazos et al. 2016; Nasiri et al. 2016; Nasiri et al. 2017), conclude that nanoparticles  
56 decrease the diffusivity of low molar mass substances. Such results suggest the applicability of  
57 the Piringer model in a migration prediction approach based on an overestimated value of  
58 diffusivity.

59 From a safety standpoint, the barrier effect provided by the nanostructure of packaging  
60 film against additives could reduce the exposure of consumers to toxic compounds and their  
61 potential adverse health effects, depending on the individual barrier properties of polymers.  
62 Although nanoclays have a positive effect on high barrier polymers such as PET, the decrease  
63 in the diffusion coefficient has no effect on the migration value for low-barrier polymers, for  
64 which the migration values are more related to the partition coefficient (Farhoodi et al., 2016).  
65 The reasons why the presence of nanoparticles decreases the mobility of the diffusing molecules  
66 are multiple. While the tortuosity effect is generally cited (Paul and Robeson, 2008; Duncan,  
67 2011), the mechanisms of diffusion in nanocomposite matrices imply additional essential  
68 factors. In the case of polymer-clay nanocomposites, the interactions of organic molecules with  
69 the clay's minerals are likely to generate a decrease in their  $D_{app}$  by sorption or adsorption  
70 mechanisms (Nasiri et al. 2016). In addition to their high cation exchange capacity, clays can  
71 exchange other chemical bonds, such as van der Waals interactions, or hydrogen bonding, with  
72 migrants, delaying their transport in the nanocomposite structure (Aguzzi et al., 2007). It is also  
73 well established that the presence of clay nanoparticles structurally modifies polymer networks,  
74 having nucleating effects, and their ability to increase the crystallization rate of semi-crystalline

75 thermoplastic polymers (Ke et al., 1999; Yuan et al., 2006). At a finer scale, crystallinity  
76 gradients in the vicinity of nanoparticles can have a modulating effect on the transfer properties  
77 of plastic-based nanocomposites (Wurm et al., 2010). This combination of effects emphasized  
78 nanocomposite bioplastics (Charlon et al. 2015b), but to our knowledge, no research has  
79 measured and characterized migration from bio-nanocomposite packaging. Such materials, by  
80 definition unstable, may behave differently than synthetic polymers in contact with food, and  
81 their inertial properties remain undemonstrated. This study aims to characterize the food contact  
82 suitability of bio-nanocomposite packaging films. In view of their emergence on the market and  
83 their environmental benefits (Rajan et al., 2018; Hongsriphan and Pinpueng, 2019), two distinct  
84 polymers: poly(butylene succinate-co-butylene adipate) (PBSA) and poly(hydroxybutyrate-co-  
85 hydroxyvalerate) (PHBV) were selected on the basis of their differing transfer properties, in  
86 order to cover different behaviors in contact with food simulants, the PHBV being a high-barrier  
87 polymer (Crétois et al., 2014) contrary to PBSA (Phua et al., 2013). Organo-modified  
88 montmorillonite was added to these materials, which were spiked with a panel of target  
89 migrating substances and submitted to migration tests following the protocol for testing  
90 conventional plastic packaging. The approach aims to measure and identify the influence of  
91 nanoclays on the diffusion properties of these emerging packaging materials.

## 92 **2 Materials and Methods**

### 93 **2.1 Materials**

94 Poly(butylene succinate-co-butylene adipate) (PBSA, PBE 001, density  $1.24 \text{ g.cm}^{-3}$ ) and  
95 Poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV, PHI 002, density  $1.23 \text{ g.cm}^{-3}$ ) pellets were  
96 commercially procured from Natureplast, France.

97 Cloisite 30B (C-30B), an organo-modified montmorillonite clay containing a methyl bis-  
98 2-hydroxyethyl ammonium quaternary salt with a cation exchange capacity (CEC) of 90

99 meq/100 g, were supplied by BYK additives & instruments, Germany. C-30B was chosen  
100 because of its favorable interaction with PBSA (Sinha Ray et al., 2008) and PHBV (Carli et al.,  
101 2011; Iggui et al., 2015).

102 An array of solid and liquid additives was chosen. These molecules represent a range of  
103 categories of chemical compounds with a variety of chemical and physical properties as  
104 described in FDA and EFSA regulations (Food and Drug Administration, 2006; European Food  
105 Safety Authority, 2011). The additives chosen include: volatile polar organic substances,  
106 volatile non-polar organic substances, non-volatile polar organic substances, and non-volatile  
107 non-polar organic substances. Three high molar mass additives and eight low molar mass  
108 additives were procured from Sigma-Aldrich (Table 1).

## 109 **2.2 Preparation of bio-nanocomposite films**

110 PBSA and PHBV films with 5 wt% C-30B were synthesized by a melt extrusion process  
111 using an EuroLab 16XL co-rotating twin-screw extruder (Thermo Scientific<sup>TM</sup>, Germany) with  
112 a L/D ratio of 40 and a screw diameter of 16 mm. The extruder produced films using a calendar  
113 die. Polymer pellets were dried at 60°C for 15 hours before use to remove residual moisture.  
114 Nanoclays were used without drying, because hydrated nanoclay platelets intercalate better with  
115 the polymer matrix (Tenn et al., 2013).

116 PBSA films were produced in three stages (Charlon et al. 2015a). First, a masterbatch of  
117 15 wt% C-30B was prepared. The polymer pellets and nanoclays were introduced in the  
118 extruder at a flow rate of 0.85 kg.h<sup>-1</sup> and 0.15 kg.h<sup>-1</sup>, respectively. The feed to die temperature  
119 profile was 120°C to 160°C. At the extrusion die, the emerging polymers were cooled in a water  
120 bath and pelletized. The masterbatch was then diluted with neat polymer to obtain 5 wt%  
121 nanoclay pellets. Finally, films of 180 ± 10 μm for PBSA and 220 ± 25 μm for PBSA  
122 nanocomposite (PBSA NCP) were produced from these pellets using a flow rate of 1.0 kg.h<sup>-1</sup>

123 and a 100°C to 135°C temperature profile. All steps were processed at a screw speed of 200  
124 rpm.

125 PHBV films were produced in two stages (Iggui et al., 2015). A masterbatch of 15 wt%  
126 C-30B was prepared in the same way as for PBSA, however with a temperature profile of 140°C  
127 to 180°C. The masterbatch was diluted with neat polymer to obtain PHBV films containing  
128 5 wt% nanoclay. The films of  $145 \pm 20 \mu\text{m}$  for PHBV and  $140 \pm 10 \mu\text{m}$  for PHBV NCP were  
129 produced using a screw speed of 210 rpm and a flow rate of  $1.0 \text{ kg}\cdot\text{h}^{-1}$ . PBSA and PHBV pellets  
130 or films were oven dried at 60°C for 15 hours after each stage and before storage.

131 The control samples of neat PBSA and PHBV were prepared following the same protocol  
132 used for nanocomposites in order to respect the same thermal processes.

### 133 **2.3 Spiking of neat and nanocomposite films**

134 The procedure used for the spiking of films depends on additive molar mass. High molar  
135 mass additives were introduced to films during the extrusion process because of their excellent  
136 thermal stability (Mauricio Iglesias, 2009). The theoretical additive amount was 500 ppm. Low  
137 molar mass additives were introduced to films through contamination at 40°C for 7 days under  
138 rotary agitation. The theoretical additive amount was 500 ppm for all low molar mass additives  
139 apart from toluene at 1000 ppm.

### 140 **2.4 Food simulants**

141 Two different food simulants were chosen to evaluate the  $D_{\text{app}}$  of the selected additives:  
142 95% ethanol, and iso-octane, which both simulate fatty foods behaviors according to the  
143 European Commission for food contact materials (EU 10/2011) (Commission, 2011). The  
144 experiments were also performed using 3% acetic acid to simulate acidic food behavior, but the  
145 migration of high molar mass additives in this solvent was less than the limit of detection.

## 146 **2.5 Desorption tests**

147 Desorption tests were carried out by putting contaminated films in contact with food  
148 simulants in a surface/volume ratio of  $6 \text{ dm}^2 \cdot \text{L}^{-1}$ . The bottles were stored under magnetic  
149 agitation at  $40^\circ\text{C}$  for 10 days, except for PHBV films contaminated by high molar mass  
150 additives, for which storage was increased to 30 days. Over specific periods of time, an aliquot  
151 of each food simulant was collected and analyzed by chromatography (GC-FID for low molar  
152 mass additives or HPLC for high molar mass additives). The samples of iso-octane were  
153 evaporated under nitrogen and re-dissolved in 100% ethanol before HPLC analysis.

## 154 **2.6 Small angle X-ray diffraction (SAXS)**

155 SAXS experiments were performed using an “in-house” setup to study the degree of  
156 exfoliation of the nanoclays in the polymer matrix. A high brightness low power X-ray tube,  
157 coupled with aspheric multilayer optic (GeniX<sup>3D</sup> from Xenocs) delivered an ultralow divergent  
158 beam (0.5 mrad; flux:  $20 \text{ MPhotons} \cdot \text{s}^{-1}$ ;  $\lambda = 1.5418 \text{ \AA}$ ; size at sample:  $0.6 \times 0.6 \text{ mm}$ ). A  
159 transmission configuration was used and the scattered intensity determined by a 2D pixel  
160 “Pilatus” detector at a distance of 1.9 m from the sample. Glass capillary support was used in  
161 the case of nanoclay powder, while for films, the beam passed through five stacked film  
162 thicknesses. The obtained intensities were corrected by transmission and the empty cell  
163 contribution was subtracted. The interlayer spacing relative to nanoclay platelets was  
164 determined at a diffraction angle in the range of  $0.5^\circ$  to  $10^\circ$ .

## 165 **2.7 Transmission electron microscopy (TEM)**

166 A JEOL 1200EX2 transmission electron microscope with 100 kV acceleration voltage  
167 equipped with an EMSIS Olympus camera was used to analyze film samples and observe



168 nanoclay dispersion and exfoliation in the polymer matrix. For that, the film samples were  
169 included in a resin and cut with a Leica UC 7 ultramicrotome.

## 170 **2.8 Differential scanning calorimetry (DSC)**

171 A differential scanning calorimeter (DSC series Q200, TA Instruments) was used to study  
172 the crystallinity of the films. Experiments were carried out on neat and nanocomposite films,  
173 before and after 10 days of contact with 95% ethanol or iso-octane. All measurements were  
174 performed under a nitrogen atmosphere. Specimens of 5-8 mg, weighed using a microbalance  
175 (Sartorius micro PRO 11), were placed in aluminum sample pans. The thermal protocol was  
176 defined according to the polymer. The PBSA samples were: heated from ambient temperature  
177 to 40°C, cooled to - 35°C, heated to 150°C, maintained at 150°C for 5 min, cooled to - 35°C,  
178 heated to 150°C, and finally cooled to 40°C. In the case of PHBV, samples were: heated from  
179 ambient temperature to 40°C, cooled to - 30°C, heated to 200°C, maintained at 200°C for 5  
180 min, cooled to - 30°C, reheated to 200°C, and finally cooled to 40°C. Temperatures were  
181 adjusted at a rate of 10°C.min<sup>-1</sup>. The apparent melting enthalpy ( $\Delta H_m$ ) was determined from  
182 the DSC curves using the Universal Analysis 2000 software by TA Instruments. The  
183 crystallinity degree ( $X_C$ ) of neat and nanocomposite polymers was determined by the equation:

$$184 \quad X_C(\%) = \frac{\Delta H_m}{\Delta H_m^0} \times \frac{100}{w} \quad (1)$$

185 Where:  $\Delta H_m$  is the melting enthalpy of the polymer matrix,  $w$  is the polymer weight fraction  
186 in the sample and  $\Delta H_m^0$  is the theoretical melting enthalpy of the polymer assumed to be 100%  
187 crystalline,  $\Delta H_m^0 = 146.0 \text{ J.g}^{-1}$  for PHBV (Barham et al., 1984) and  $\Delta H_m^0 = 116.9 \text{ J.g}^{-1}$  for PBSA  
188 (Nikolic and Djonlagic, 2001).

## 189 **2.9 Sorption of food simulants**

190 The food simulant uptake by the films was determined by gravimetric measurements  
191 using a precision balance ( $10^{-4}$  g) before and after subjecting films to contact with food  
192 simulants at 40°C for 10 days under magnetic agitation. At the end of this procedure, excess  
193 food simulant was removed with tissue paper before re-measuring. The percentage of solvent  
194 uptake was obtained by the following equation:

$$195 \text{ Sorption} = \frac{m_t - m_i}{m_i} \times 100 \quad (2)$$

196 Where:  $m_i$  and  $m_t$  are weights of samples before and after sorption, respectively.

## 197 **2.10 Gas chromatography with flame ionization detector (GC-FID)**

198 An Agilent 7890A GC equipped with a 7693A Automatic Sampler and a flame ionization  
199 detector was used to determine the concentration of low molar mass additives ( $< 400 \text{ g.mol}^{-1}$ )  
200 in food simulants. The components were separated using a HP-5 (5%-  
201 phenyl)methylpolysiloxane capillary column of 32 mm ID and 30 m length. The thermal  
202 protocol used for the oven was as follows: an initial temperature of 40°C maintained for 5 min,  
203 heated at a rate of  $6^\circ\text{C.min}^{-1}$  to 270°C, maintained for 15 min. The injector temperature was  
204 250°C. An external calibration was made in each food simulant in the range of 1.25 –  
205 40  $\text{mg.L}^{-1}$ .

## 206 **2.11 High performance liquid chromatography (HPLC)**

207 An Alliance HPLC system (Waters) equipped with an Alltima C18 column (250 mm  $\times$   
208 2.1 mm, 5- $\mu\text{m}$ ) protected with a Alltima C18 (7.5mm  $\times$  2.1 mm, 5- $\mu\text{m}$ ) column guard was used  
209 to determine the concentration of high molar mass additives in food simulants. Compounds  
210 were separated with 55% acetonitrile at a flow rate of  $0.3 \text{ mL.min}^{-1}$  at 50°C. Absorbance was

211 recorded at 230 nm to quantify the additive concentration. An external calibration was made in  
212 each food simulant with concentrations of 1.25 to 20 mg.L<sup>-1</sup>.

## 213 **2.12 Estimation of the D<sub>app</sub>**

### 214 **2.12.1 Fick's second diffusion equation**

215 The D<sub>app</sub> of additives from the polymer films into food simulant was calculated from  
216 experimental desorption kinetic curves using Fick's second law. The films are considered as  
217 one-dimensional infinite plane sheets, given that diffusion via the borders of the films is  
218 negligible. Applying Fick's second law results in the following one dimensional diffusion  
219 equation:

$$220 \quad \frac{\partial C}{\partial t} = D_{app} \left( \frac{\partial^2 C}{\partial x^2} \right) \quad (3)$$

221 Where: C is the additive concentration, t, the contact time, x, the position in the film and D<sub>app</sub>,  
222 the apparent diffusion coefficient.

223 The Eq. (3) was solved using the following initial (Eq. 4) and boundary (Eq. 5) conditions:

$$224 \quad C(t = 0, x) = C_0 \quad \forall x \in [-L, L] \quad (4)$$

$$225 \quad C(t, x = \pm L) = C_s(t) \quad \forall t \geq 0 \quad (5)$$

226 Where: C<sub>s</sub>(t) is the additive concentration in food simulant at time t and L, the film half  
227 thickness.

228 This diffusion model can be used provided that the following assumptions are verified  
229 (Helmroth et al., 2002): (i) additive contamination of the film is homogeneous, (ii) there is no  
230 noticeable swelling caused by interaction between the food simulant and the polymer, (iii) there  
231 is no concentration gradient in the food simulant, and (iv) the film thickness is homogeneous.  
232 In the case of an infinite plane sheet suspended in a stirred solution of limited volume, the Eq.  
233 (3) can be solved analytically as described by Crank (Crank, 1975):

234 
$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} \exp\left\{-\frac{D q_n^2 t}{L^2}\right\} \quad (6)$$

235 With:

236 
$$\alpha = \frac{1}{K_{P,F}} \frac{V_F}{V_P} \quad (7)$$

237 Where:  $M_t$  is the total amount of additives in food simulant at time  $t$  and  $M_\infty$  is the total amount  
 238 of additives in food simulant at the steady state,  $V_P$  is the polymer volume and  $V_F$  the food  
 239 simulant volume,  $(q_n)_n$ , the positive roots of the equation  $\tan q = -\alpha q$  and  $K_{P,F}$ , the partition  
 240 coefficient of the additive in the polymer/food simulant system.

241 The numerical simulations were carried out using Matlab® software and its *lsqnonlin*  
 242 function to estimate the  $D_{app}$ . To evaluate the correlation between experimental and estimated  
 243 data, the percentage of the root mean-square error (% RMSE) was calculated using the  
 244 following equation:

245 
$$RMSE = \frac{1}{M_0} \sqrt{\frac{1}{N} \sum_{i=1}^N ((M_t)_{\text{experimental}} - (M_t)_{\text{predicted}})^2} \times 100 \quad (8)$$

246 Where:  $M_0$  is the initial mass of additive in the biopolymer film and  $M_t$  is the mass of additive  
 247 in the food simulant at time  $t$ .

### 248 **2.12.2 Piring correlation**

249 The Piring correlation (1994) estimates the worst case additive diffusivity in a given  
 250 polymer by correlating the diffusion coefficient with the molar mass of additives and the  
 251 temperature.  $D_P$  (Eq. 9) can be refined to not depend on experimental data (Brandsch et al.,  
 252 2002).

253 
$$D_P = D_0 \exp\left[A_P - 0.1351 M^{\frac{2}{3}} + 0.003 M - \frac{10454}{T}\right] \quad (9)$$

254 With:  $D_0 = 10^4 \text{ cm}^2 \cdot \text{s}^{-1} = 1 \text{ m}^2 \cdot \text{s}^{-1}$  and  $A_P = A'_P - \frac{\tau}{T}$

255 Where the parameter  $A_p$  is linked to the polymer and describes the basic diffusion behavior of  
256 the polymer matrix in relation to the migrants,  $M$  is the molar mass of the additive,  $T$  is the  
257 absolute temperature and  $\tau$  is a polymer specific “activation temperature” increment. The  
258 apostrophe ' indicates the parameter is temperature independent.

259 The parameters  $A'_p$  and  $\tau$  are given in Table 2 (Begley et al., 2005). In the absence of  
260 specific parameters for PBSA and PHBV, those for LDPE and PET were used for, respectively,  
261 low and high barrier property polymers.

## 262 **3 Results and discussion**

### 263 **3.1 Microstructure of composite material**

264 Because the interaction between polymers and nanoclays determines the formation of  
265 exfoliated nanocomposite materials, clay modification has been extensively studied (Muñoz-  
266 Shugulí et al., 2019). Exfoliated nanoparticles reduce diffusion by creating tortuosity effect and  
267 results in higher transfer properties (Nasiri et al. 2016).

268 The degree of exfoliation of nanoclay platelets in biopolymer matrices was measured by  
269 XRD (Fig. 1 A) and TEM (Fig. 1 B). As expected, the analysis of the C-30B powder by XRD  
270 revealed a diffraction peak at  $4.9^\circ$ , corresponding to an interlayer spacing of 1.8 nm (Bharadwaj  
271 et al., 2002). The analysis of neat biopolymers exhibited no diffraction peaks in the studied  $2\theta$   
272 angle range, while the analysis of nanocomposites revealed one diffraction peak with a shift  
273 towards the smallest angles compared to C-30B powder,  $2.7^\circ$  for PBSA NCP and  $2.2^\circ$  for  
274 PHBV NCP, which respectively corresponds to a d-spacing of 3.3 nm and 4.0 nm. Similar  
275 values were reported for PBSA NCP (Charlon et al., 2015a) and PHBV NCP (Bordes et al.,  
276 2008). This increase in the interlayer distance reflects the formation of intercalated structures,  
277 confirmed by TEM observations which indicated both intercalated and exfoliated structures for  
278 nanocomposite materials.

### 279 **3.2 Migration curves of additives from studied films into food simulants**

280 The desorption kinetic of each additive from polymers into food simulants was measured  
281 over time, until 10 days, or 30 days in the case of PHBV contaminated with high molar mass  
282 additives. An example of desorption kinetics is reported in Fig. 2, for methyl stearate additive,  
283 from neat and nanocomposite PBSA into 95% ethanol food simulant.

284 For all molecules, a good correlation was observed between migration experimental data  
285 and simulated curves using Eq. (6), with a RMSE inferior to 6%, calculated using Eq. (8).

286 Desorption curves can be analyzed in their growth phase, from which the diffusion  
287 coefficient can be estimated, and in their state of equilibrium, from which the partition  
288 coefficient can be estimated. The addition of nanoclays in the polymer matrix has varying  
289 effects on both phases according to the nature of the diffusing additives (Nasiri et al. 2016).

### 290 **3.3 Comparison of the $D_{app}$ of additives in neat and nanocomposites materials**

291 The estimation of the  $D_{app}$  of each additive from biopolymer into food simulant is reported  
292 in Fig. 3, with the respective impacts of: polymer type, food simulant, and the effect of  
293 nanoparticle incorporation.

294 The differences in the  $D_{app}$  in the various systems, illustrated by the differing scales of  
295 the histograms, reflect the influences of the polymer type and the food simulant in contact. As  
296 in previous works that highlight the poor gas barrier properties of PBSA (Phua et al., 2013), the  
297 diffusivity values measured in PBSA are between five and twenty times lower than those in  
298 PHBV, which normally has good barrier properties (Crétois et al., 2014).

299 Contact with 95% ethanol seems to have a dramatic impact: producing diffusion values  
300 nearly ten times higher than for iso-octane contact. The very peculiar behavior of polyesters in  
301 contact with ethanol was already reported for PET (Begley and Hollifield, 1990), PLA  
302 (Jamshidian et al., 2012), and PHBV (Chea et al., 2015).

303 For PBSA and PHBV matrices with nanoparticles in contact with 95% ethanol and iso-  
304 octane, the  $D_{app}$  varies according to additives. The impact of nanoparticles is not significant if  
305 compared to the impact of the biopolymer type or food simulant in contact. For PBSA in contact  
306 with 95% ethanol, nanoparticles decreased the  $D_{app}$  for all additives. In contact with iso-octane,  
307 nanoparticles increased the  $D_{app}$ , especially for low molar mass additives. For PHBV,  
308 nanoparticles increased the  $D_{app}$  significantly whatever the food simulant in contact.

309 These results contradict previous conclusions on conventional synthetic materials. For  
310 polyurethane, there is a negative correlation between C-30B (concentrations 0 - 50 wt%) and  
311 the diffusivity of three volatile organic compounds: toluene, decane, and butanol (Herrera-  
312 Alonso et al., 2009). Nasiri et al. (2016) measured the diffusivities in LLDPE with a wide range  
313 of additives exposed to four food simulants:  $D_{app}$  decreased with the addition of Cloisite  
314 regardless of the nature of the diffusing substance. Therefore, whereas plastic-based  
315 nanocomposite materials meet inertia criteria regarding the migration of low molar mass  
316 substances, the behavior of biodegradable materials raises new concerns relating to compliance  
317 with regulations and consumer safety. Given the limited available data, it is difficult to establish  
318 behavioral laws to describe the specific impact of nanoclays on the evolution of the  $D_{app}$  of low  
319 molar mass additives. In addition to the tortuosity effect demonstrated in section 3.1, these  
320 results suggest that nanoparticles modify polymer structures (size, shape, or arrangement of  
321 spherulites, and degree of crystallinity) and thus their transfer properties.

### 322 **3.4 Predicting the $D_{app}$ of additives according to molar mass**

323 The  $D_{app}$  of additives is related to their specific volume and, consequently, to their molar  
324 mass:  $D \sim M^{-\alpha}$  with a scaling parameter  $\alpha$  that can be related to the transport mechanism  
325 (Lodge, 1999).

326 Fig. 4, below, shows the  $D_{app}$  of additives in function of their molar mass in neat and  
327 nanocomposite PBSA (Fig. 4 A) and PHBV (Fig. 4 B) in contact with 95% ethanol and iso-  
328 octane food simulants. The linear dependence of  $\text{Log}(D) = f(M)$  is clearer for PBSA than  
329 PHBV. The dependence of the diffusion coefficient on size has already been demonstrated in  
330 natural rubber and in a glassy synthetic polymer (Chern et al. 1985; Reynier et al. 2001;  
331 Martinez-Lopez et al., 2016). The inclusion of nanoparticles does not contradict this  
332 relationship given their weak influence on additive diffusivity.

333 Log D being correlated with the molar mass of additives, a Piringer correlation can be  
334 applied to PBSA and PHBV biopolyesters. This empirical model would enable verification of  
335 accordance with European regulations of suitability for food contact of materials on the basis  
336 of an overestimation of the diffusion coefficient of plastic additives.

337 Lacking the specific parameters,  $A'_p$  and  $\tau$ , for PBSA and PHBV, the regression was  
338 performed using the values for LDPE and PET, these two polymers being selected as references  
339 for their low and high barrier properties respectively (Arora and Padua, 2010). The curves  
340 obtained from the Piringer model using key parameters of LDPE and PET are presented in  
341 Fig. 4. Migration modelling can provide the upper migration values, necessary to predict a  
342 reliable worst-case scenario for bio-polyesters. While the PET Piringer model underestimates  
343 the diffusivity values measured of bio-polyesters, the LDPE model is better adapted, slightly  
344 overestimating diffusivity (except for high molar mass additives), especially for neat and  
345 nanocomposite PBSA in contact with 95% ethanol. The values of  $A'_p$  and  $\tau$ , although based on  
346 the integration of large quantities of experimental data are insufficient to provide Piringer  
347 parameters guaranteeing systematic overestimation of migration levels from PHBV and PBSA  
348 based packaging. However, the results of this study suggest that the incorporation of nanoclay  
349 does not modify these recommendations.

350



### 351 **3.5 Impact of the sorption of food simulant**

352 The contact of polymers with food simulating liquids can modify their transport  
353 properties (Figge, 1972), and the presence of nanoparticles is likely to impact these interactions.  
354 The sorption of food simulant by the semi-crystalline biopolymer usually induces swelling in  
355 the biopolymer, which accelerates additive migration and increases the diffusion coefficient  
356 value (Reynier et al., 2001; Barnes et al., 2007).

357 The solvent uptake of PBSA, PHBV and their corresponding nanocomposites after 10  
358 days of contact with 95% ethanol and iso-octane at 40°C were summarized in Table 3. The  
359 sorption of ethanol by both tested packaging films could explain the high  $D_{app}$  values measured  
360 during the contact with this food simulant (Fig. 3).

361 In the case of PBSA based materials, significant ethanol uptakes of 3.5% (neat) and 4.7%  
362 (nanocomposite) were recorded, although there was no measurable change in film thickness.  
363 The 95% ethanol sorption value of PHBV is in accordance with the value reported by Chea et  
364 al. (2015) on the same matrix/food simulant system. As mentioned in section 3.3, the peculiar  
365 interaction of 95% ethanol with polyesters was already proven with PET (Begley and Hollifield,  
366 1990; Widén et al., 2004; Kim and Lee, 2012), PLA (Jamshidian et al., 2012) and PHBV (Chea  
367 et al., 2015).

368 For neat and nanocomposite PBSA in contact with iso-octane, no solvent uptake was  
369 detected. Neat and nanocomposite PHBV in contact with iso-octane had a < 1.5%, solvent  
370 uptake.

371 The incorporation of nanoclays in the polymer matrix leads to different behaviors  
372 depending on the nature of the food simulant. 95% ethanol uptake increased with nanoclays  
373 whatever the polymer. In PHBV, addition of nanoclay reduced iso-octane uptake. Nanoclays  
374 are hydrophilic and therefore soluble in ethanol (Ho and Glinka, 2003) which leads to a greater

375 solvent uptake. However, we cannot attribute the increase in  $D_{app}$  values observed for all  
376 additives solely to solvent sorption.

### 377 **3.6 Impact of the semi-crystalline structure of bio-nanocomposites**

378 Bio-nanocomposite transfer properties are influenced by factors such as the degree of  
379 crystallinity of the polymer: high crystallinity limits movement and therefore limits the  
380 diffusion of migrating substances (Hedenqvist et al., 1996).

381 The degrees of crystallinity of neat and nanocomposite biopolymers evaluated by DSC  
382 experiments on films without contact and after 10 days in contact with food simulants at 40°C  
383 were summarized in Table 4.

384 PHBV has a high degree of crystallinity (Chea et al., 2015): almost twice that of PBSA,  
385 which may explain the difference between  $D_{app}$  values for these two materials.

386 The degree of crystallinity of polymers proved to be food simulant dependent. In contact  
387 with 95% ethanol, the degree of crystallinity decreases by 1.3% for PHBV, and by 3.9% for  
388 PBSA. These results are similar to previous research conducted on these polymers and food  
389 simulants (Chea et al., 2015; Siracusa et al., 2015). The decrease in crystallinity could be  
390 attributed to the degradation of polymer chains due to hydrolysis reactions induced by the 95%  
391 ethanol. However, in contact with iso-octane, there was no change in the degree of crystallinity  
392 for PHBV, a 1.3% increase for PHBV NCP and a close to 2% increase for neat and  
393 nanocomposite PBSA. This result confirms the findings of Chea et al. (2015): there was no  
394 structural change to PHBV in contact with iso-octane.

395 C-30B decreases the degree of crystallinity of the two polymers by nearly 10%. This  
396 has previously been observed for PBSA/C30B (Sinha Ray et al., 2005), and for PHBV/OMMT  
397 (Wang et al., 2005). It can be explained by the full exfoliation of nanoclays platelets in the  
398 polymer matrix (see section 3.1), which restricts the mobility of the polymer chains and thus  
399 prevents them from crystallizing (Krikorian and Pochan, 2003). This decrease results in an

400 increase of the amorphous phase in which the diffusivity of additives is facilitated, this tendency  
401 is observed in all cases apart from PBSA in 95% ethanol (Fig. 3).

402 Although the degree of crystallinity of materials is known to impact the transport  
403 properties of semi-crystalline polymers, strict correlation between crystallinity and diffusivity  
404 cannot be concluded in the case of biodegradable packaging materials. For instance,  $D_{app}$  of  
405 additives in PBSA are three times higher in contact with 95% ethanol than with iso-octane, but  
406 the crystallinity of both materials is similar. The relationship between diffusion and crystallinity  
407 on a macroscopic scale remains obscure. Nanoclays generate localized crystalline gradients  
408 (Wurm et al., 2010) which could modify the transport properties of materials.

#### 409 **4 Conclusion**

410 The incorporation of nanoclays in biodegradable materials raises new questions related  
411 to their food contact suitability. While the few studies carried out on synthetic plastic materials  
412 agree that the inclusion of nanoclays decreases diffusivity, this work demonstrates that this is  
413 not the case for biodegradable materials. The presence of nanoparticles affects diffusion  
414 variously, depending on the nature of the migrating substance and particularly depending on  
415 the nature of the food simulant. As previously observed for biopolyester based materials,  
416 contact with ethanol, whose diffusion activation mechanisms remain unclear, is the worst-case  
417 scenario. This particular sensitivity of biopolyesters to ethanol, especially when they  
418 incorporate inorganic nanoparticles such as nanoclays, underscores the problem of applying  
419 existing recommended testing conditions for the evaluation of conventional plastic materials to  
420 these new materials. Ethanol sorption, which promotes the crystallization of synthetic  
421 polyesters and thus prevents the mobility of low molecular weight molecules, appears to be  
422 enhanced by the incorporation of clay nanoparticles. Being necessarily cautious we cannot, with  
423 sufficient accuracy, predict migration levels from bio-nanocomposite packaging using diffusion  
424 models generally applied to food contact material considered as continuous homogeneous

425 phase. However, Piringer's empirical model remains an applicable way to overestimate  
426 migration and guarantee consumer safety. This model would be more effective with the creation  
427 and inclusion of database of the diffusion coefficients of low molecular weight molecules in  
428 these materials.

429

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#### 434 Compliance with ethical standards

435 The authors declare that there is no conflict of interest regarding the publication of this paper.

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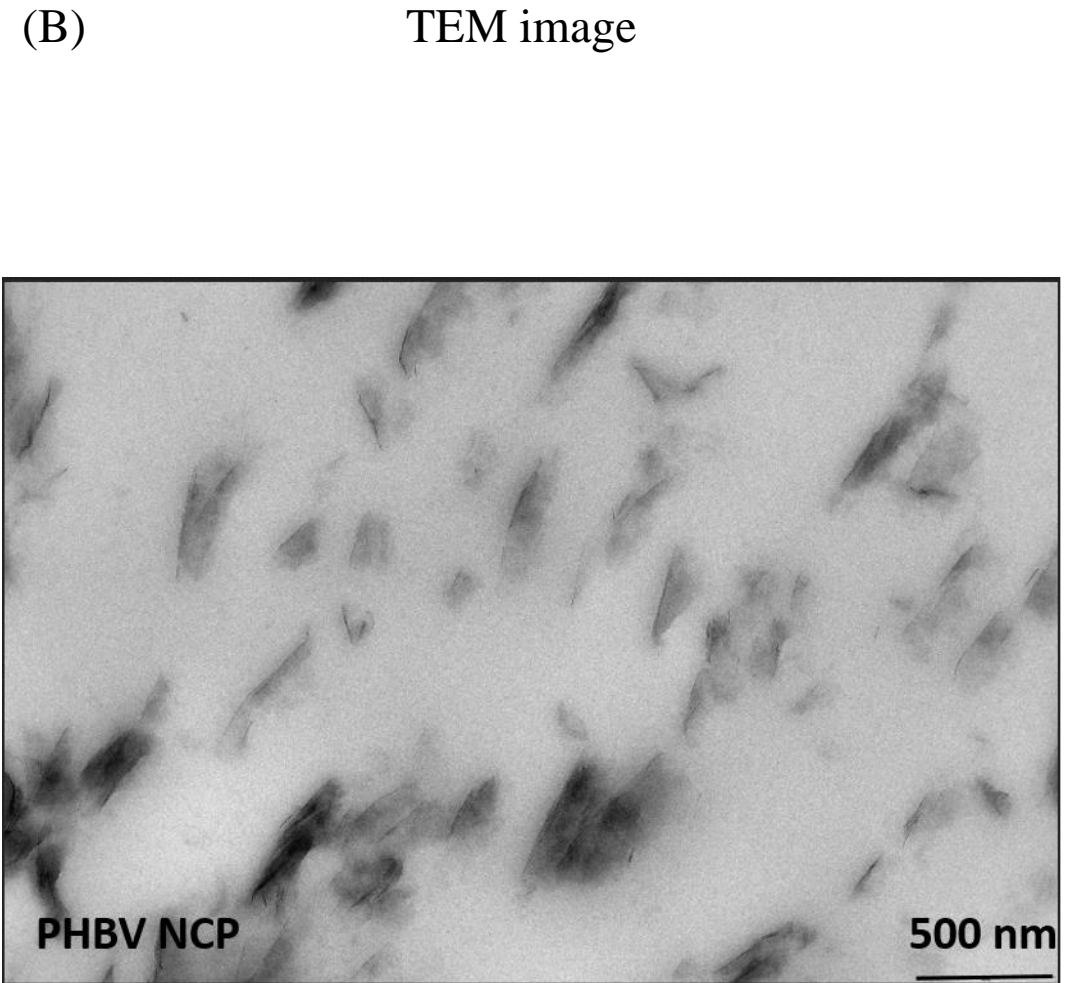
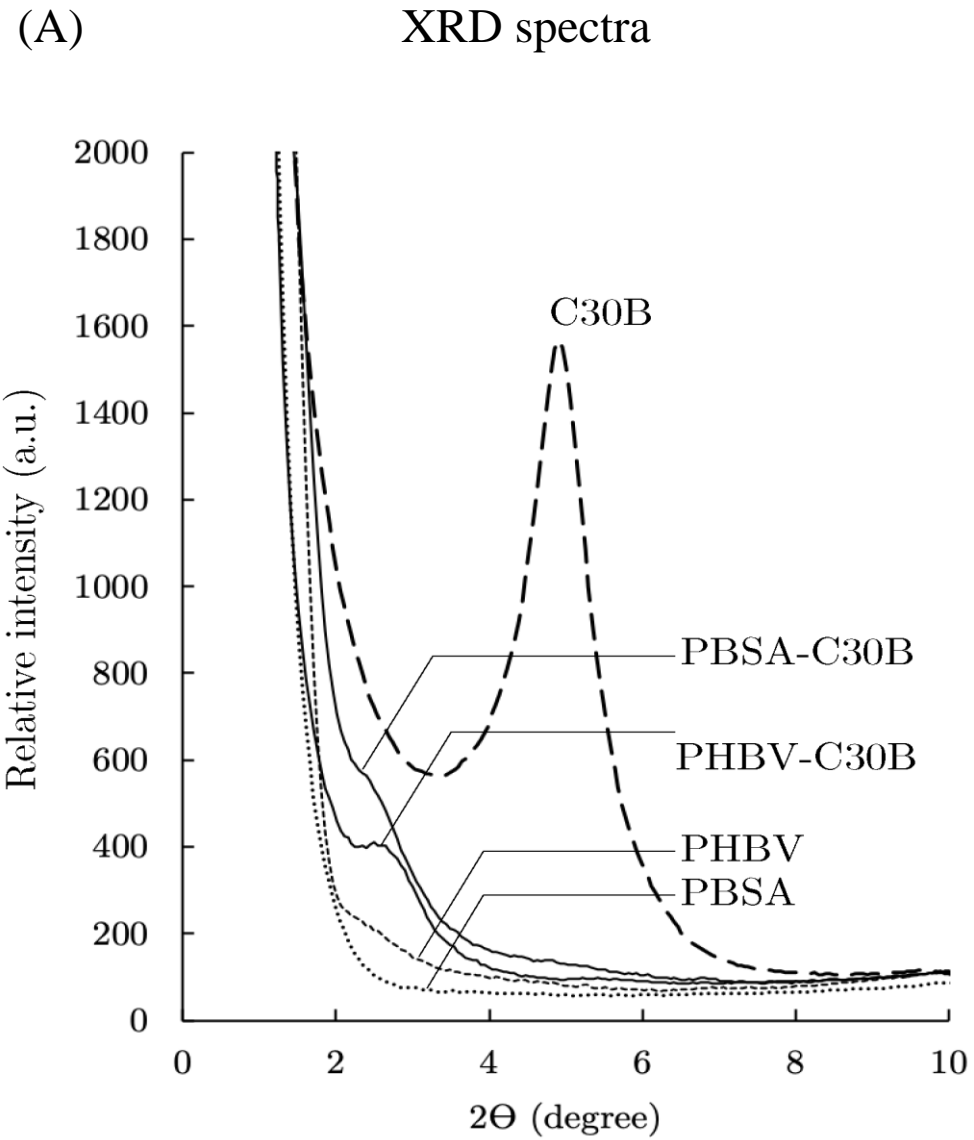
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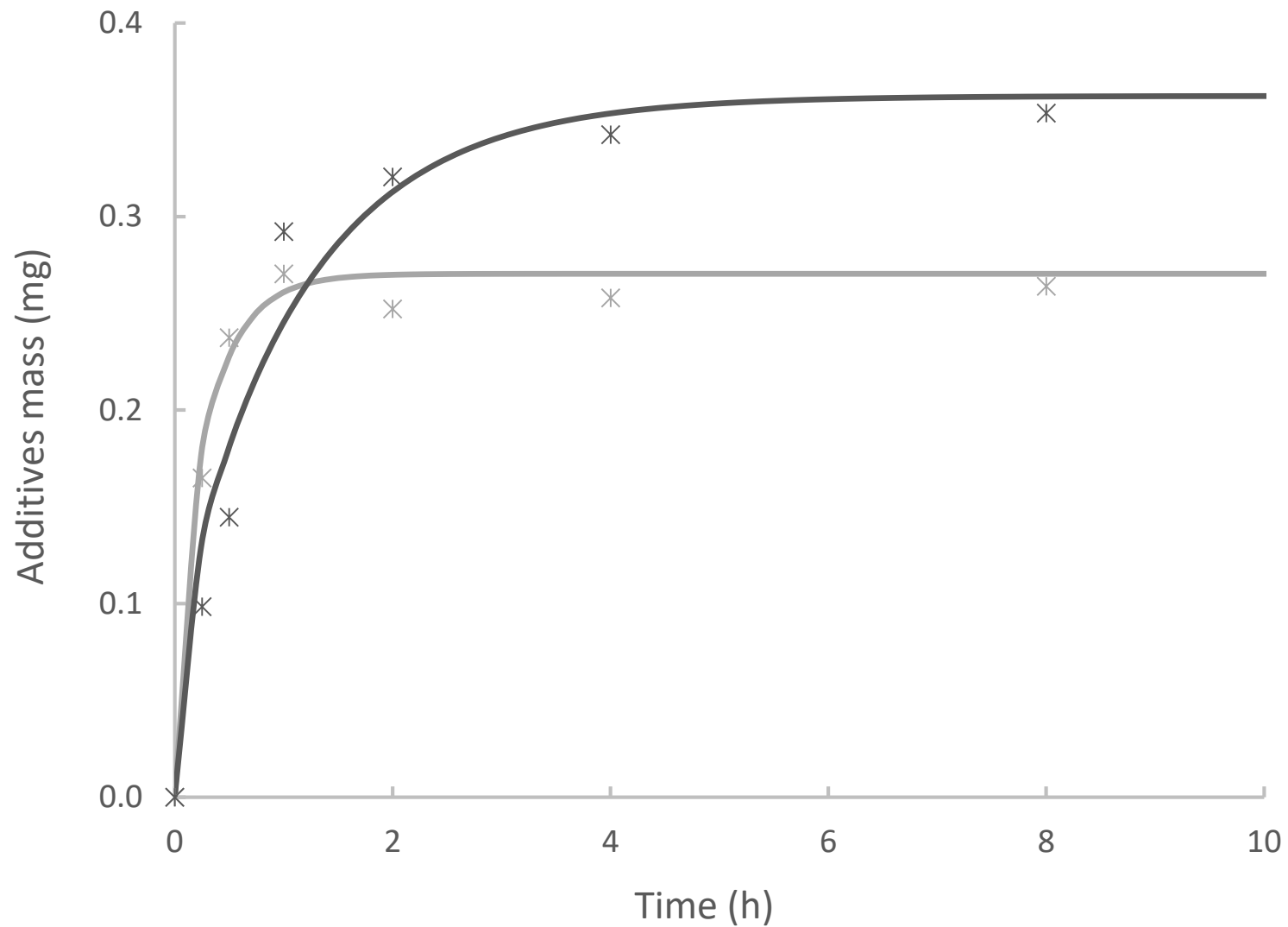
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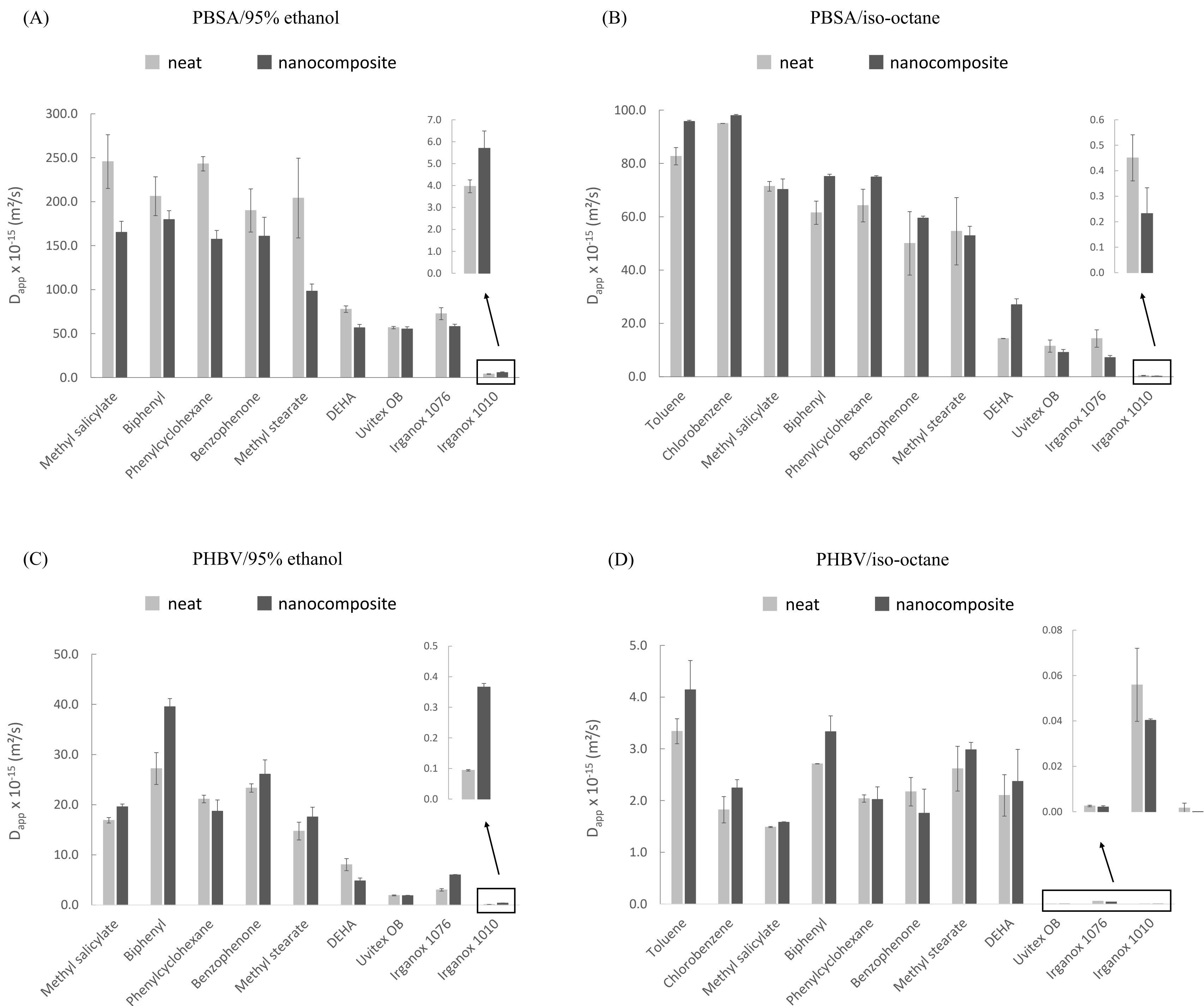
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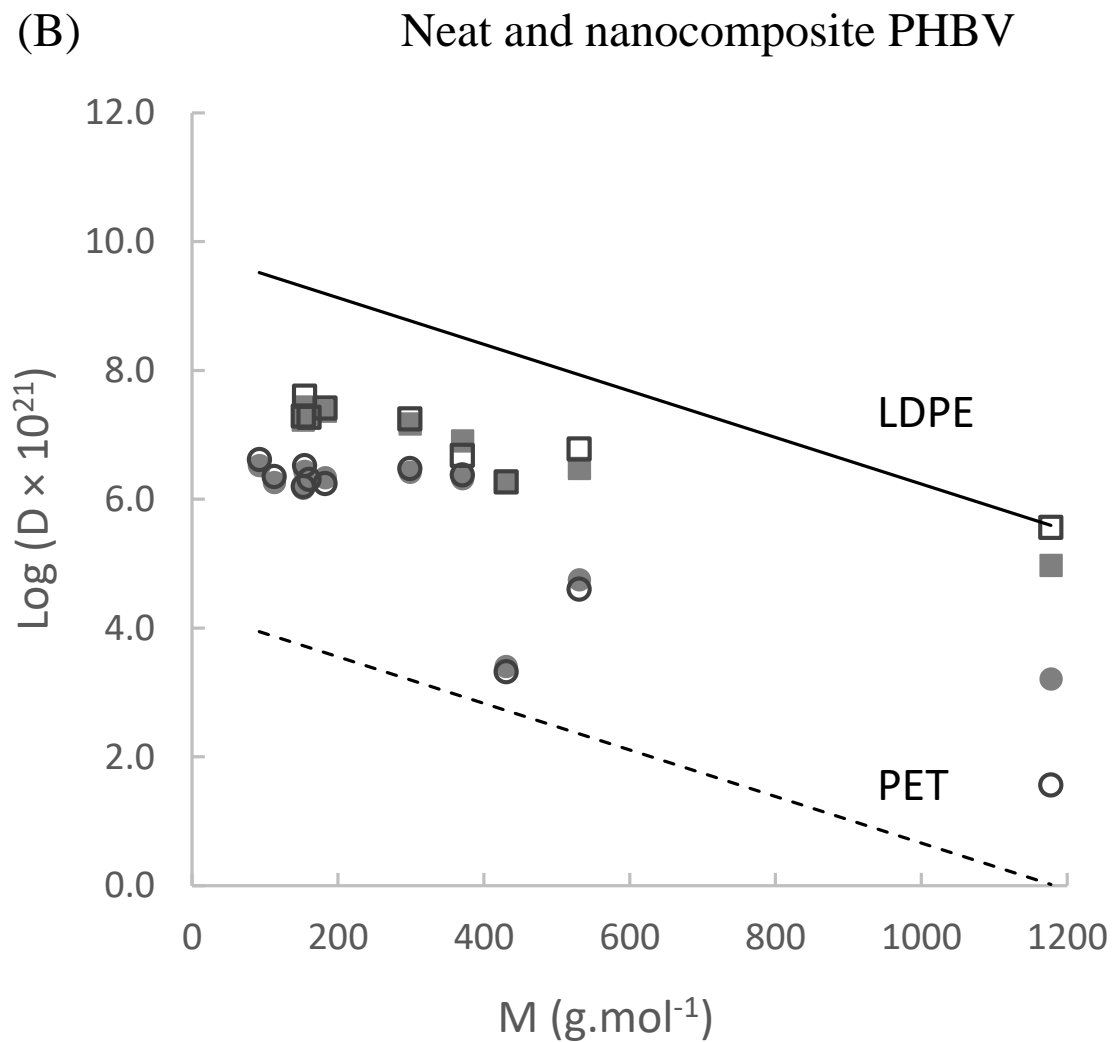
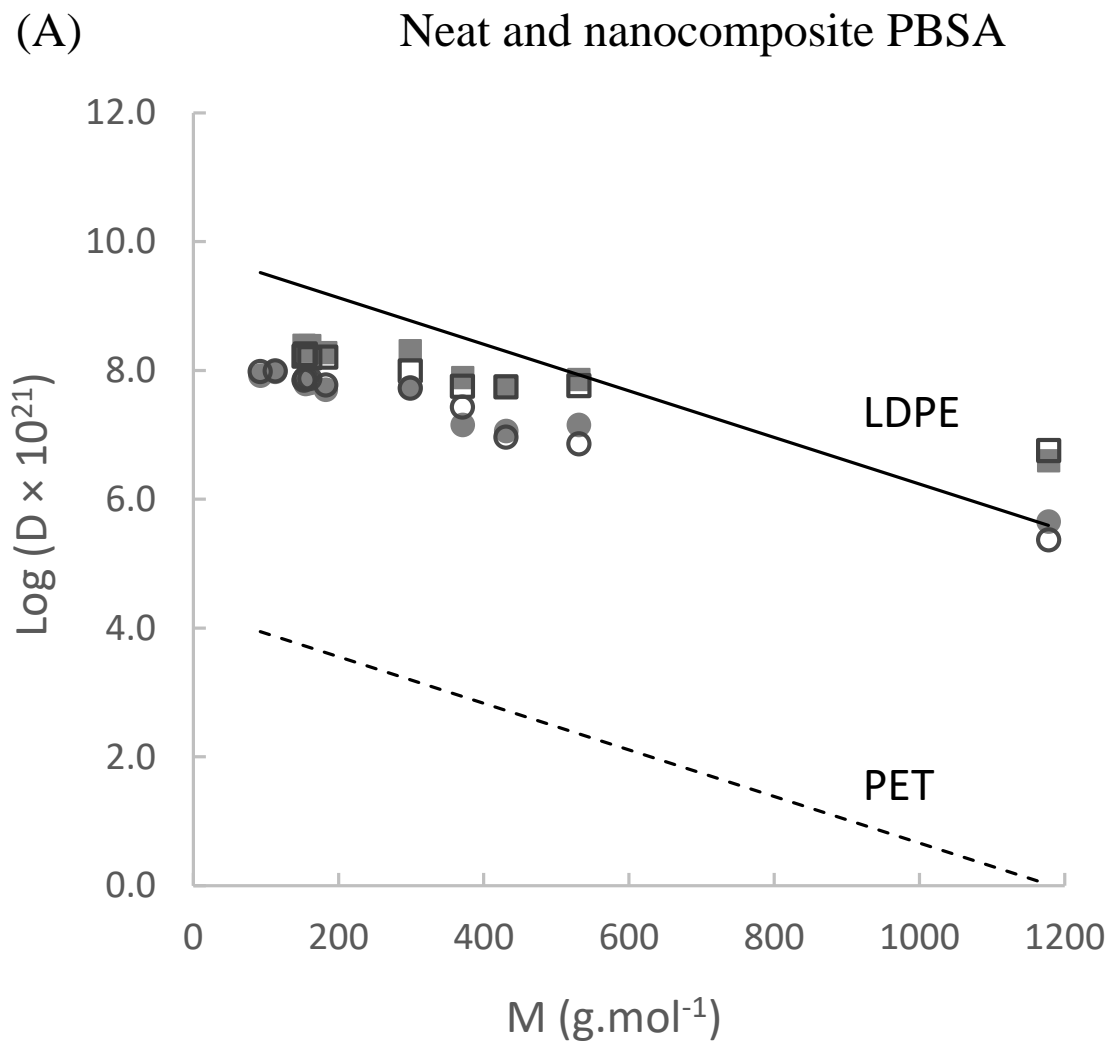
**Fig. 1.** XRD spectra of neat and nanocomposite polymers (A) and TEM image (B) of PHBV NCP.



**Fig. 2.** Experimental (symbols) and simulated (curves) desorption kinetics for the first 10 hours for PBSA (grey) and PBSA NCP (black) into 95% ethanol for methyl stearate.



**Fig. 3.** Comparison of  $D_{app}$  of additives in neat (grey bars) and nanocomposite (black bars) PBSA (Fig. A and B) and PHBV (Fig. C and D) films in contact with food simulants: 95% ethanol (Fig. A and C) and iso-octane (Fig. B and D).



**Fig. 4.**  $D_{\text{app}}$  of additives in function of additives molar mass for neat and nanocomposite PBSA (A) and PHBV (B). Neat PBSA or PHBV in contact with 95% ethanol (■) or iso-octane (●) and PBSA NCP or PHBV NCP in contact with 95% ethanol (□) or iso-octane (○). Piringer estimations in LDPE (—) and PET (---) at 40°C.

Table 1: List of selected additives.

Category	Code	Physical properties	CAS number	M (g.mol <sup>-1</sup> )
High molar mass contaminants	Uvitex OB	Non-volatile	7128-64-5	430.56
	Irganox 1076	Non-volatile polar	2082-79-3	530.86
	Irganox 1010	Non-volatile	6683-19-8	1177.63
Low molar mass contaminants	Toluene	Volatile non-polar	108-88-3	92.14
	Chlorobenzene	Volatile polar	108-90-7	112.56
	Methyl salicylate	Non-volatile polar	119-36-8	152.15
	Biphenyl	Volatile non-polar	92-52-4	154.21
	Phenyl cyclohexane	Non-volatile non-polar	827-52-1	160.26
	Benzophenone	Non-volatile polar	119-61-9	182.22
	Methyl stearate	Non-volatile non-polar	112-61-8	298.50
DEHA	Non-volatile polar	103-23-1	370.57	



Table 2: LDPE and PET specific parameters.

Polymer	$A'_p$	$\tau$
LDPE	10	0
PET	2.2	1577

Table 3: Solvent uptake of films after 10 days of contact with food simulant at 40°C.

Sample	Solvent uptake (%)	
	95% ethanol	Iso-octane
PBSA	3.7 ± 0.5	0
PBSA NCP	4.7 ± 0.1	0
PHBV	3.5 ± 0.1	1.3 ± 0.1
PHBV NCP	3.8 ± 0.2	0.5 ± 0.1

Table 4: Degree of crystallinity of film samples without contact and after 10 days of contact with 95% ethanol or iso-octane at 40°C.

Sample	Degree of crystallinity (X <sub>c</sub> ) (%)		
	Without contact	95% ethanol	Iso-octane
PBSA	38.2 ± 0.0	36.7 ± 0.1	39.0 ± 0.1
PBSA NCP	34.9 ± 0.4	34.1 ± 0.3	35.7 ± 0.1
PHBV	62.8 ± 1.6	62.0 ± 0.1	62.9 ± 0.1
PHBV NCP	55.0 ± 0.4	53.6 ± 0.3	55.7 ± 0.1