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Multi-faceted Migration in Food contact Polyethylene-based Nanocomposite packaging

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ABSTRACT:

The flourishing market of nanocomposite food packaging has raised concerns about the safety of these materials. While several works on this issue have been published in recent years, they main focus in these studies was found to be on the possible migration of the nanoparticle its constituents. However, thorough safety evaluation of these materials would not be realistic until the nano-packaging system would be regarded as a whole with all of its components and the interactions of all these components. This matter is specifically crucial in terms of the interaction of nanoparticles with the non-nano additives which are added during the packaging processing. As the toxicity of these processing additives is no less than the nanoparticles, the possible impact of the nanoparticles on the transfer properties of these substances could play a decisive role on the risk assessments of the nanocomposite for food application. This study is an attempt through a thorough analysis of nanocomposite risks in terms of the interactions of components and the resulting effects on the release of nanocomposite substances. In this regard a model nanocomposite of LLDPE and nanoclay which is also comprised of intercalants and some selective additives were put in contact with various food simulants were considered and the

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global, specific and elemental exposure to the substances were extensively evaluated. The results are believed to provide more tenable judgements about the safety of polymer nanocomposites.

KEYWORDS: Clay Polymer Nanocomposite, Multi-dimensional Migration, Food contact materials regulations

1. Introduction

To comply with shelf-life requirements, polymer nanocomposites (PNC) have emerged in the past decade as a new class of food packaging materials which provides several advantages, such as enhanced mechanical, thermal and barrier properties of conventional plastic packaging or improved function of active (antimicrobial) and intelligent materials (Farhoodi, 2016; Gontard et al., 2017). Particular interest is that such improvement in nanocomposite properties are achieved with very low loading levels (typically up to 5% by weight) of nanoparticles while these properties are not commonly attained with less than 25-40 wt% loading in the microcomposites (Chaudhry et al., 2017).

However, besides the advantages of nanocomposite application, their safety issue should be taken into consideration especially for food packaging systems, because of the potential adverse effects of nanoparticles on human health. Nevertheless, the "safety aspects" in most of recent researches are considered in respect to the potential migration of nanoparticles from different polymers to several foods and in diverse conditions of contact time/temperature (Metak et al., 2015) or to the toxicity of these nanoparticles for human health and environment (Gaillet and Rouanet, 2015; Sajid et al., 2015).

In viewpoint of the regulations, scarce rules could be found due to the lack of information on the risk assessment of nanoparticles, and even among these regulations there is not a consensual management on the usage of nanoclay in Food Contact Materials (FCM). According to the Food and Drug Administration (FDA), montmorilonite (Mt) is considered as GRAS (Generally Recognized As Safe, under the section 21CFR184.1155) and can be consequently used in food packaging formulation (Molinaro et al., 2013). This statement is based on the *in vitro* studies indicating the cytotoxic effects of clay minerals in case of exposure to a high dose (e.g.

53 thousands of ppm), which is unlikely to happen for human being (Li et al., 2010; Baek et al.,
54 2012).
55 In contrast, the European Food Safety Authority (EFSA) in a recent guidance on the risk
56 assessment of nanotechnologies in the food and feed chain (Hardy et al., 2018) considered that
57 the scientific knowledge remains too limited today to define a threshold for the migration of
58 nanomaterials from FCM. As consequence, EFSA recommend that "an argument for safety may
59 be made on a case-by-case basis if migration of a nanomaterial in particulate form is only in
60 trace amounts".
61 Among the engineered nanomaterials used in packaging placed on the market, Mt is already
62 widely employed to improve the barrier properties (oxygen and carbon dioxide permeability) of
63 conventional materials. Mt is the main component of bentonite which is included in the list of
64 authorized substance (No 393) of the Regulation (EU) 10/2011 (European Commission, 2011)
65 without restriction. Recently the EFSA Panel on FCMs, enzymes, flavorings and processing aids
66 (CEF) has amended a scientific opinion on the use of montmorillonite clay in FCMs which
67 concludes that inclusion of nanoclay up to 12% w/w do not represent a health risk because of the
68 absence of potential migration (EFSA Panel on Food Contact Materials, Enzymes, 2016). In
69 spite of the published guidance on the safety evaluations of nanomaterials, the scientific
70 committee on emerging and newly identified health risks reported these procedures could be
71 expected to be remained under development until there would be sufficient information available
72 to characterize the possible harmful effects on human and the environment (Williams, 2006;
73 Wyser et al., 2016).
74 The toxicity and exposure to the nanoparticles are crucial factors in evaluating the risks related to
75 their food packaging application, by limiting the studies to these two aspects, several other

sources of risks being still ignored. In order to better apprehend the risks of nanocomposites for such application, an exhaustive investigation must include additional components and their interactions. In a simplistic view, the nanocomposite packaging in contact with food could be considered to comprise three main component systems *i.e.* polymer, nanoparticles and food. However, several other additives (plasticizers, anti-oxidants, UV stabilizers, anti-static agents) are usually added to the plastic-based material during the packaging processing to further enhance their properties. Moreover, for most of inorganic nano-clays such as Mt, some other chemicals should be incorporated in the nanocomposite structure in order to disentangle the nanoparticle aggregates and consequently induce their exfoliation on one hand, and to enhance their compatibility with the base polymer in regards to the polarity on the other hand. Therefore, in an ordinary nano-packaging, a pentagon of interactions is involved between polymer, nanoparticle, food, processing additives and intercalants (the headspace volume to be considered as a possible sixth contributing part). It is worth noting that processing additives and intercalants are not considered in the same category because the type and quantity of the latter have direct and decisive effect on the efficiency of the nanocomposite as a “nano”-structure. In polymers with low polarity (such as polyolefins) the chemical modification of the polymer using a compatibilizer (adhesion promoter) such as maleic anhydride-grafted polyethylene (MA-g-PE) is necessary to promote greater interaction of the matrix with the filler and facilitate the formation of exfoliated nanocomposite structures. Although increasing the quantity of compatibilizer as well as modifier to a certain level facilitates the dispersion of nano-clay through the base polymer, these components should be examined for their migration as it should not surpass the authorized level.

98 In addition to the migration of the nanoparticles and the intercalating agents, and like any other
99 FCM, safety assessment of nanocomposite packaging must comply with the general requirement
100 of the EU regulation that define overall and specific migration limits (European Commission,
101 2011). Overall migration (OM), the total mass released by the packaging material is regarded as
102 an indicator of the food contact material inertness which sets an upper limit of 10 mg for all
103 transferred substituents per dm^2 (or 60 mg/kg food) of the food contact article. On the other
104 hand, based on the toxicological information of the molecules, the specific migration limits
105 (SML) were set out for a single component to ensure the safety of the final package.
106 Preliminary step in evaluating the safety of the nanocomposite is to determine its overall
107 migration which takes into account the total release of nanoparticle (or its components),
108 modifier, compatibilizer, residual monomers, processing additives and the non-intentionally
109 added substances (NIAS) which may be present in the nanocomposite in the form of impurities
110 in the additives, monomers and other starting substances which are used to manufacture the
111 nanocomposite.
112 The second step concerns the assessment of nanoparticle migration which has attracted the most
113 attention in the recent years and could be considered from three different perspectives:
114 Regulations, theory and experiments. So far, no evidence was found in the literature to indicate
115 that nanoclay is likely to cause adverse effects on health when used in the food packaging
116 (Piperigkou et al., 2016). However, while several studies provide some information about the
117 migration of nanoclay/nanoclay constituents, the effects of nanoclay incorporation on the
118 potential migration of chemical constituents of plastics (monomers and processing additives)
119 were not taken into consideration.

120 The third part of the nanocomposite safety evaluation is related to the migration of the
121 compatibilizer and the modifier which is of significance due to the two factors related to the
122 compliance with SML and alteration of the nature of the nanocomposite. In other words, not only
123 the migration limits of these components should be less than the values which are set out in
124 Commission Regulation (EU) No 10/2011, but also the effect of their release on the nature of the
125 nanocomposite (in terms of polarity) and the consequences on the adsorption/desorption of other
126 additives should be evaluated.
127 In the last step, the effect of the nanoparticle and its accompanying components (modifier and
128 compatibilizer) on the migration of several additives with various size, functional groups,
129 polarities and volatilities was assessed according to a specifically designed challenge test which
130 was originally recommended by EFSA to determine the decontamination efficiency of the
131 recycling process for recycled polymer packaging (EFSA, 2011).
132 As a consequence of the multiple factors involved in the safety evaluation of nanocomposite
133 packaging in terms of the exposure to various migrants, this study attempts to draw a broader
134 perspective of the possible interactions between the nanocomposite components and the release
135 of diverse substances in contact with different type of food simulants.
136

137 **2. Experimental**

138 2.1. Chemicals and food simulants

139 Linear low-density polyethylene (LLDPE, LL 1002YB melt flow index 2.0 g/10 min, density
140 0.918 g/cm3) was supplied by Exxon Mobil Chemical. Cloisite 20 (C20), a Bis(hydrogenated
141 tallow alkyl)dimethyl ammonium bentonite salt (Bulk density: 350 kg/m3; Density (20 °C): 1.80

142 g/cm3; Particle Size, D50: < 10 µm; Lamellar spacing (XRD, d001): 2.7 nm) was provided by
143 BYK Additives & Instruments.
144 Fusabond E226 (supplied by DuPont™) was chosen as the compatibilizing agent between
145 nanoclay and the matrix which is a maleic anhydride modified polyethylene (MA-g-PE) with
146 melt flow index of 1.75 g/10 min and density of 0.93 g/cm3.
147 The chemical additives comprising of three solid surrogates (biphenyl 99.5%, benzophenone
148 99% and methyl stearate 99%), five liquid contaminants (toluene 99.8%, chlorobenzene 99.8%,
149 methyl salicylate ≥ 99%, phenyl cyclohexane ≥ 97% and DEHA ≥ 99%) as well as Arquad®
150 2HT-75 (Di-hydrogenated tallow di-methylammonium chloride) and Maleic anhydride 99%
151 were all provided by Sigma-Aldrich.
152 The migration of chemicals was evaluated using 5 food simulating liquids according the EU
153 regulation 10/2011. The selected food simulants encompass 3w/v% aqueous acetic acid to
154 represent acidic food, ethanol 10% to simulate aqueous food, ethanol 50% for alcoholic foods
155 (with alcohol content of greater than 20%) as well as the dairy products and ethanol 95% and
156 iso-octane which are both representing fatty foods.
157
158 2.2. Polymer Nanocomposite (PNC) processing
159 The nanocomposite was synthesized with LLDPE as the base matrix, 5 wt% of C20 and 15 wt%
160 of MA-g-PE by melt intercalation method using a co-rotating twin screw extruder (Thermo
161 Scientific™ EuroLab 16) with a L/D ratio of 40 and a screw diameter of 16mm at screw speed of
162 200 rpm and feed rate of 1.0 kg/h.
163
164 2.3 Impregnation of PNC

165 The virgin polymer and nanocomposite were contaminated by a mixture of additive with
166 theoretical additive amount of 500–1000 ppm, which is within the range recommended by EFSA
167 (EFSA, 2011),
168 The Impregnation of PNC was performed with 80 µl of additive cocktail mixed with 25 g of the
169 polymer pellets. The bottles were sealed and stored at 40 °C under rotary agitation. After 1 week,
170 the contents were rinsed with distilled water and the contaminated pellets were divided and
171 subjected to the four chosen food simulants as well as the pure dichloromethane for extraction to
172 obtain initial concentration (C_0).
173 The polymer samples were also extracted with pure dichloromethane to evaluate the initial
174 quantity of additives (M_0) before the migration process by gas chromatography (GC-FID,
175 Agilent 7890A gas chromatograph equipped with a HP-5 capillary column of 32mm × 30m ×
176 0.25 µm).
177
178 2.4 Overall Migration Test
179 Overall migration (OM) level which represents the total amount of non-volatile substances
180 transferred from the food-contact material to the food (EU 10/2011) is determined by a
181 gravimetric method after the total immersion of neat samples in the selected food simulants
182 based on the standardized testing conditions set out for long term storage (40°C for 10 days) in
183 EU 10/2011.
184 In this regard, the neat samples were cut in disks of 3 cm diameter and then kept in a vacuum
185 oven at 50°C for 2 days. Respecting a surface/volume ratio of 6 dm^2/L of food simulant, the
186 polymer disks of a thickness of 177.4±16.1 and 143.3±8.3 µm for LLDPE and PNC respectively
187 with the total area of 60 cm^2 were weighed using a microbalance (0.1 mg resolution) prior to the

188 migration test and then placed in a 100 ml migration cell (DURAN® screw thread tubes) with
189 PTFE-sealed caps. Such a sample geometry makes it possible to neglect any migration linked to
190 a possible edge effect. Glass beads were used as spacers between the disks to ensure a proper
191 contact with the simulant. Before filling, the migration cells were blown out with nitrogen to
192 prevent any dust contamination. The cells were then filled with the respective simulants, sealed
193 and stored in a 40°C oven. Each sample/simulant combination was prepared in triplicate for the
194 migration test.
195 After 10 days of contact, the bottles were ultrasonicated for 2 min to detach any potential
196 particles from the sample surface and the glass beads. The samples then removed and placed in a
197 vacuum oven at 50°C for 3 days. After evaporation of the simulant, the specimens were weighed
198 again and eventually overall migration was calculated in milligrams per square decimeter of the
199 surface area of sample.
200
201 2.5 Specific Migration Test
202 Specific migration test was performed according to recommendation described in EU 10/2011
203 under standard conditions identical to those described for the global migration test. The
204 European legislation has published a list of substances allowed in food contact articles for which
205 the specific migration limits are assigned based on the toxicological evaluation of the substance.
206 These limits which are expressed in mg substance per kg food are 30mg/kg under the FCM
207 Substance No. 234 and No. 15 for maleic anhydride and quaternary ammonium salt, respectively
208 (European Commission, 2011). Therefore, the migration of these two components were
209 evaluated by the same experiment as for the overall migration. By the end of the contact time,

210 the simulants were collected to be analyzed by HPLC for maleic anhydride and LC-MS/MS for
211 di-hydrogenated tallow di-methylammonium chloride.
212 Except for the iso-octane, other simulants were directly injected into the HPLC and LC-MS/MS
213 system. However, iso-octane needed additional sample preparation. In this regard, the simulant
214 was evaporated to dryness by a nitrogen stream. The residue was then re-dispersed in ethanol and
215 was severely agitated on a vortex for 30 s.
216
217 2.5.1 Liquid chromatography tandem-mass spectrometry (LC-MS/MS)
218 LC-MS/MS analysis was performed on a Synapt G2-S (Waters) spectrometer equipped with a
219 positive electrospray ionization (ESI^+) source. The capillary voltage was set to 3.5 kV and the
220 sampling cone voltage was set to 60 V. Compounds were separated using a gradient of methanol
221 (solvent B) in 0.1% formic acid in water (solvent A) over 15 minutes. The gradient program was
222 set as follows: 0-2 min, 20% solvent B; 2-3 min, 20-80% solvent B; 3-5 min, 80-95% solvent B; 5-
223 13 min, 95% solvent B; and 13-15 min, 20% solvent B. Standard solutions of Arquad® 2HT-75 in
224 ethanol, with concentrations ranging from 0.1 to 10 mg/L, were used to establish the external
225 calibration curves based on the $C_{18}C_{18}$ peak areas.
226
227 2.5.2 High Performance Liquid Chromatography (HPLC)
228 Maleic anhydride concentration in simulants was analyzed by Alliance HPLC with a reversed
229 phase Alltima C18 column (250 mm ×2.1 mm, 5-µm packing) protected with a guard column of
230 Alltima C18 (7.5mm × 2.1 mm, 5-µm packing). Compounds were separated using isocratic
231 elution with acetonitrile/water/phosphoric acid 30:70:0.1 (v/v/v). Elution flow rate was
232 maintained at 0.2 mL/min and UV detection was recorded at 240 for ethanol 95% and pure

233 ethanol and 254 nm for other simulants based on the maximum absorption. External calibration
234 was established in each simulant with concentrations of 0.1 to 100 mg L^{-1}.
235
236 2.6 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)
237 Migration of nanoclay elements from the nanocomposite to the simulants was investigated by
238 ICP-MS method. Elemental analysis measurements for Al, Si and Mg were carried out with a
239 quadrupole ICP-MS instrument (iCAP Q, Thermo Scientific), equipped with a concentric
240 nebulizer and a quartz cyclonic spray chamber connected to the ICP-torch for sample
241 introduction. Before instrumental analysis, an acid digestion procedure is applied on the samples.
242 After putting the neat samples in contact with the simulants for 10 days at 40ºC, the samples
243 were separated from the liquid and the simulants were evaporated under a nitrogen stream and
244 re-dissolved in HNO_3 1%. Blanks of the food simulants were also undergone the same
245 procedure. All migration solutions were prepared in triplicate
246
247 2.7 Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM/EDX)
248 Simulants were examined for the presence of (nano)particles as well as their elemental
249 composition by SEM/EDX. In this regard, the simulants (after 10 days of contact with NC) were
250 filtered through a Whatman Anodisc membranes with 0.2 µm pore size and 47 mm diameter.
251 The filtrate liquid then passed through the Anodisc membranes with 0.02 µm pore size. The
252 membranes were put in petri dishes to be dried in room temperature for 48 hours and covered
253 with perforated aluminum foil to avoid the absorption of dust. After simulant evaporation,
254 SEM/EDX analysis was carried out on the membranes using the EDAX attachment (Oxford
255 Instruments) of the Hitachi S-4500 I SEM (Hitachi High Technologies America, Inc.,
256 Schaumburg, USA).

3. Results and discussion

3.1 Overall migration

Determining the overall migration of all components from the packaging is a key factor which is typically conducted by the manufacturer or food packager to ensure the compliance with European regulatory limit which is 10 mg/dm^2 on a contact area basis or 60 mg/kg in the simulant or food. The global migration values for pure polymer and the PNC are reported in Figure 1.

The total migration measured from PNC is higher than the corresponding values in pure polymer, however, in viewpoint of the FCM safety, it is out of consideration as far as the values are below the regulated limit. Although the OM value seems to transgress the limit in case of the PNC contact with iso-octane, it should be pointed out that the contact condition applied in this study for iso-octane is 10 days at 40ºC for the sake of the comparison with other simulants and consequently higher than the recommended conditions of the European commission (2 days at 20ºC) for checking the compliances with FCM regulations. Moreover, iso-octane represents a very extreme condition as a food simulant due to the strong interaction between iso-octane and the polymer. It was reported in the literature that even the contact duration of 2 hours at 40 ºC with this simulant results in a far greater migration than the 10 days of contact with olive oil at the same temperature (Baner et al., 1992). The emphasized OM value in this simulant is largely due to the iso-octane migration front which is penetrating into the polymer and is highly depended on the nature of the polymer as well as the applied contact time.

Though the compliancy of overall migration in nanocomposites with the regulatory limits mitigates the safety concerns about the application of these materials, it is of interest to recognize the reasons for the elevated OM of nanocomposites in comparison to the pure PE. The mismatch

of the overall migration values with the sum of specific migration of nanoclay elements, modifier and compatibilizer, implies that the increased migration in nanocomposite can be explained by various comconmitting effects including (1) migration of oligomeric compounds from the partial degradation of LLDPE, (2) migration of additives (antioxidant type in particular) initially introduced into the commercial polymer fraction or (3) migration of impurities present in the sample of Cloisite 20A.

In addition and as evidenced by literature, the nanocomposite structure is prone to be affected by the stimulated thermo-oxidative degradation of polymer due to the nanoclay incorporation during melt-blending process. The rate of thermo-oxidative degradation was found to be increased by the oxygen-scavenging effect due to the char formation in the clay surface as well as the catalytic activity of the acidic active sites created by the Hoffman decomposition of the alkyl quaternary ammonium ions (Annamalai and J. Martin, 2014). During thermal degradation proceeding according to the Hofmann degradation mechanism the ammonium cation loses an olefin and an amine and leaves an acid proton on the surface of the Mt. This acid site on the surface of Mt has a catalytic effect during the initial stages of decomposition of organic material within the organo-modified nanoclay (Leszczyńska et al., 2007).

It should be noted that although the synthesized nanocomposite in this work was exposed to 160-180ºC in the extruder, which is just before the onset decomposition temperature of the alkyl quaternary ammonium ions (Xie et al., 2001), the masterbatch method of synthesis could trigger more degradation by heat dissipation due to the combined effects of higher filler content and higher melt viscosity (Shah and Paul, 2004). Moreover, the heat barrier effect of nanoclay could provide superheated conditions inside the polymer melt leading to extensive random scission of polymer chain and evolution of numerous chemical species which, trapped between clay layers,

303 have more opportunity to undergo secondary reactions. As a result, some degradation pathways
304 could be promoted leading to enhanced charring (Leszczyńska et al., 2007).

305 Another factor contributing to the polymer degradation is the presence of compatibilizer. Melt
306 processing of PE with PE-g-MA is considered to ease PE chain scission (Esteki et al., 2013) or
307 initiating some other side reactions (crosslinking) which would cause some changes in the
308 molecular structure of the polymer (Rzayev, 2011).

309

310 3.2 Migration of nanoclay modifier and compatibilizer

311 The presence of maleic anhydride as a compatibilizer between nanoclay and LLDPE lowers the
312 surface energy of nanoclay and improves the wetting characteristics of the polymer which
313 consequently leads to a better dispersion of nanoclay in the polymer. However, in European
314 legislation, a group restriction was specified for this substance which indicates that the total
315 specific migration limit ($SML_{(T)}$) for the sum of substances applicable to this group should be
316 less than 30 mg/kg (European Commission, 2011). As it is demonstrated in Table 1, the
317 migration of the compatibilizer is far below the specific limitation for this substance.

318 The migration process can be described as the result of the diffusion of chemical additives
319 through the polymers and the desorption of the diffused molecules from the polymer surface to
320 the food or food simulants. In addition to the transport properties of a component (*i.e* diffusivity
321 and freedom of movement which could be restricted by obstruction effect of the nanoparticles),
322 the migration of organic molecules such as intercalants and compatibilizer, additionally depends
323 on their respective affinity for both the food simulants and PNC. The polarity of diffusing
324 molecules therefore appears as a determining factor of food contamination.

325 The results reported in Table 2 demonstrated a main influence of the nature of food simulant
326 with higher migration values observed for fatty food simulant. Regarding the migration of maleic
327 anhydride which exhibits a hydrophilic character, no tendency towards iso-octane was noted due
328 to the difference in nature in terms of their polarity. The migration of maleic anhydride proved to
329 be dramatically enhanced in ethanol 95% that can be explained by a modification of polymeric
330 structure due to the sorption of ethanol by the LLDPE-based material and subsequent increase of
331 substance diffusivity.
332 Nanoclay modifiers such as quaternary alkyl ammonium is primarily used to increase the
333 nanoclay interlayer space, however, once the nanoclay were embedded into the polymer, the
334 modifier may be released from the nanoclay surface into the polymer matrix during the polymer
335 processing or when the nanoclay was in contact with the solvent due to the solvent penetration
336 into the polymer matrix. This part of modifier is considered as "free" and its release may follow
337 the diffusion behavior of small molecules within the polymer matrix due to the presence of free
338 volume and polymer chain relaxation (Yining et al., 2014).
339 The migration of modifier from the PNC is demonstrated in Table 2 for all simulants. As
340 mentioned above, it could be inferred that in contact with iso-octane and ethanol 95%, the
341 simulant easily penetrates the polymer, swells the matrix and interacts with the modifier, which
342 leads to the higher release of modifier in comparison to other simulants.
343 However, the results of this study is not in accordance with the EFSA opinion on modified Mt, in
344 which migration of dimethyl dialkyl (C16-C18) ammonium compounds from polyolefins was
345 not detected in ethanol 95% with a LOD of 6 µg/kg (EFSA Panel on Food Contact Materials,
346 Enzymes, 2016). Nevertheless, even in the condition of this study, the migration of the modifier

347 is less than the 30 mg/kg which is regulated under FCM No. 15 for "alkyl, linear with even
348 number of carbon atoms (C12-C20) dimethylamines" (European Commission, 2011).
349
350 3.3 Migration of Nanoclay or their elementary building blocks
351 Study of the transport of engineered nanoparticles (ENM) within nanocomposite and its release
352 into different food is crucial in the safety assessment of the PNC. In addition to a possible
353 contamination due to the mechanical erosion of the PNC, ENM release phenomena during the
354 life cycle of nanocomposite could be taken place by diffusion, desorption and dissolution that
355 could be accelerated by the degradation of the polymeric matrix. Although multiple processes for
356 nanomaterial release may simultaneously occur, the main release process depends on where the
357 nanomaterial is located, the extent to which it interacts with the surrounding media, its ability to
358 migrate through the host matrix material (size and steric hindrance), and whether the particle
359 remains an ENM or is transformed into ionic form (Noonan et al., 2014). The nanoclay used in
360 this study is montmorillonite (*i.e.* bentonite), which is a natural 2:1 layered phyllosilicate (de
361 Abreu et al., 2009; Hannon et al., 2015) exhibiting an average thickness of ~1nm and average
362 lateral dimensions ranging from a few tens of nm to several µm. Each platelet contains a layer of
363 aluminum or magnesium hydroxide octahedral sandwiched between two layers of silicon oxide
364 tetrahedral, with the ideal formula (full unit cell) of $M^{+}_{0.66}Si_8Al_{3.34}Mg_{0.66}O_{20}(OH)_4$ in which M^{+}
365 represents the cation charges in the interlayer (Uddin, 2018). As Si, Al and Mg are the 3 main
366 elements of the nanoclay, the migration of these elements into the food simulants are measured
367 by ICP-MS and represented in Figure 2.
368

369 Considering the safety limits for the migration of metallic element and in spite of the well-
370 developed knowledge on their toxicity and assignment of the provisional tolerable intake (1
371 mg/kg bw/week (Panel on Food Additives, Flavourings, 2016) & 250 mg/person/day (European
372 Food Safety Authority, 2006) for Al and Mg respectively), the specific requirements for metals
373 in food contact materials specified in Annex II of the Regulation EU/10/2011 does not include
374 any specific restrictions for these constitutive elements. Therefore, their use must comply with
375 the appropriate national laws of each Member State regarding their release. However, Council of
376 Europe Resolution CM/Res(2013)9 on 'metals and alloys used in food contact materials and
377 articles', has recommended the specific release limits (SRL) of 5 mg/kg food for aluminum,
378 whereas no limits for Si and Mg was defined (Europe, 2013). Yet, comparing the extensive
379 application of nanoclays, few researches have addressed the release of nanoclay constituents.
380 The summary of previous studies performed on the migration of nanoclay elements is presented
381 in Table 1 (Avella et al., 2005; Simon et al., 2008; Mauricio et al., 2010; Schmidt et al., 2011;
382 Farhoodi et al., 2014; Maisanaba et al., 2014; Huang J.-Y. A4 - Chieng, Y. Y. A4 - Li, X. A4 -
383 Zhou, W., 2015; Echegoyen et al., 2016).
384 It can be pointed out that most of these investigations have been performed on biosourced and/or
385 biodegradable materials which exhibits a high-water sensitivity. In these cases, the contact with
386 liquid food simulant proved to enhance the migration of elements in higher extent than in
387 polyolefins.
388 The investigation shows very low levels of migration of the three measured mineral elements. As
389 it is evidenced, the migration of Si is higher than the other components for all food simulants
390 which is due to the abundance of Si at the clay surface. It could be assumed that dissolved silica
391 may be generated either by removal of edge-exposed tetrahedral groups (surface hydrolysis) or

392 by diffusion of silica through the interlayer space of an expanded Mt. There exists a general
393 agreement that dissolution progresses by breaking of bridge oxygen bonds, Si–O–Al, at the
394 crystal edges (Rozalén et al., 2008). That means that Mt dissolve inwards from the edges, which
395 has been confirmed by AFM observations (Bickmore et al., 2001).
396 External stimuli that would likely affect ENM surface bonds include liquid characteristics (pH,
397 ionic strength, and presence of contaminants that promote bonding), temperature, physical
398 abrasion and vibration. These external factors could dislodge ENMs from the food contact
399 material surface and enable them to release to the simulant. Considering the impact of pH, it is
400 widely known that Al is preferentially released in acidic solutions (Cama et al., 2002). In
401 agreement with this statement, no significant release of aluminum from PNC was observed in the
402 food simulants excepted for acetic acid 3%. However, it should be noted that the demonstrated
403 levels represent the worst case as the polymer was undergone the total immersion which implies
404 that the migration level also includes the release from cut edges. The release of the migrant from
405 the edges, as opposed to the comparatively larger surface area of the faces is assumed to be small
406 for thin films of sufficient diameter, but whether this assumption holds for nanoparticles, which
407 may be more likely to be manually dislodged by the cutting process, is not yet clear.
408 The results of element migration illustrated once again the main influence of food simulant on
409 the migration extent. In addition to the difference in concentration, the relative proportion of
410 each element proved to be variable and dependent on the food simulant. Considering the
411 computation of formula weight of Mt, a unit weight of one clay of 367 $g.mol^{-1}$ includes 112
412 $g.mol^{-1}$ of Si, 45 $g.mol^{-1}$ of Al and only 8 $g.mol^{-1}$ of Mg. The fact that the released quantity did
413 not match this elemental distribution demonstrated that Mt do not migrate under undamaged

form but probably undergoes structural modification during the contact with food simulant and suggest a migration of elements in whole or in part under ionic form.

This issue is of high importance regarding the safety point of view because of the possible interactions of released elements. For instance, high concentration of aluminum would be neurotoxic and increase the risk of cognitive impairment and dementia (Gillette-Guyonnet et al., 2007). However, several studies (Edwardson et al., 1993; Bellés et al., 1998; Parry et al., 1998) claimed that silicon acts as an antidote to aluminum toxicity by reducing the bioavailability of aluminum. These results could further abate the concerns of aluminum release from the nanoclay PNCs.

In regard to iso-octane, although there is no tendency for the clay elements to be released in the food simulant, it should be noted that due to the "aggressive" nature of this simulant towards polyethylene, there could be many other components which are leaving the polymer in contact with iso-octane. By leaving the polymer, these products could cause the silicate to migrate to the sample surface which eventually facilitate its release to the simulant.

Although ICP-MS provides valuable information on the migration of nanoclay elements, it gives no indication about the migration of nanoparticle *per se*. Theoretically, nanoclay particles have the potential to release from nanocomposites in contact with food. However, the release process of nanoclay particles may be different due to their size difference and specific chemistry. From a kinetic point of view, the migration of Mt from polyolefin material could be considered as negligible. The slow rate of transfer due to the large size of Mt in comparison with the other spherical nanomaterials exhibiting a radius in the order of magnitude of 1 to 4 nm such as nanoparticle of silver, iron, zinc of titanium (Simon et al., 2008; Bott et al., 2014; Störmer et al., 2017). To the best of our knowledge, only one investigation evidenced the migration of nano-

437 clays in nanoform released from the surface of the polymer film (Echegoyen et al., 2016). In the
438 study by Schmidt et al. (Schmidt et al., 2011), although the particles ranging from 50-800 nm
439 were detected in 95% ethanol food simulant, none of the characteristic clay minerals were
440 detectable after acid digestion and the analysis by ICP-MS suggested that the detected particles
441 were not of nanoclay origin. In addition, even physical and mechanical surface stresses do not
442 seem to induce migration of inorganic particles such as Laponites, whose structure is close to
443 that of Mt, to be of concern (Bott and Franz, 2019). The results of other studies did not show any
444 nanoclay in the extracts, although it could be argued that this is due to the limitations of the
445 technology rather than the absence of nanoparticles (Chaudhry et al., 2008). One of the
446 techniques that could be applied to detect nanoparticles is SEM-EDX. However, knowing the
447 resolution of the EDX probe (~ 1 μm), it should be noted that this method could identify the
448 agglomeration of nanoclay sheets (in the case of probable migration).
449 As several contamination sources could contribute to the migration results, at the first place, the
450 SEM-EDX of nanoclay powder was acquired and shown in Figure 3 which reveals the majority
451 presence of the constituent elements of the clays but also the occurrence of impurities such as
452 iron or chlorine initially present in the commercial fraction.
453 Based on the EDX results, the atomic ratio of Si/Al and Si/Mg are 2.4±0.1 and 17.1±1.2,
454 respectively. However, for the further particle analysis of the simulants which are filtered
455 through Anodisc membranes, Si/Mg ratio was chosen as the marker because the membrane
456 contains aluminum which could contribute as the background in the EDX results. Some of the
457 SEM-EDX results for the particles detected in filtered simulants are demonstrated in Figure 4.
458

Although according to the Figure 4 many particles are found in the simulants, Si/Mg ratio does not comply with corresponding ratio in the nanoclay powder. Therefore, either of the conclusions could be obtained accordingly; 1. All the detected particles are external contaminants and the nanoclay in the form of nanoparticle per se has not migrated through simulants or the size of the released particles are less than the detection limit of SEM-EDX (1 μm). 2. Some of the demonstrated particles are representative of the agglomeration of the nanoclays, however, the ratio of elements has been changed through the 10 days of contact due to the dissolution of some elements.

3.4 Additive Migration

During the production of food contact materials, several processing additives are used to improve thermal, optical and mechanical properties of plastic materials. Moreover, during their usage in contact with food, some components may be formed due to the decomposition of the plastic packaging. In the case of nanocomposites, some additional factors would take part in the migration of these additives. In order to understand these interactions, it should be specified that how much of these additives could migrate to the food in a “worst case” scenario, and how could the nanoclay affects the migration of these substances. This issue has already been investigated on high-barrier polymers such as PET (Farhoodi et al., 2017) or PA (de Abreu et al., 2010) to demonstrate the beneficial effects of the barrier effects of nanoclays. This question is worth asking for a low-barrier polymer such as LLDPE for which the incorporation of inorganic nanoparticles can differently modulate the inertness properties.

481 The migration of organic compounds was measured on a panel of 8 low molecular weight
482 molecules representatives of possible migrants in food-packaging (solvent, wetting agent,
483 plasticizer and photo-initiator in UV-radiation) selected on the basis of the Scientific Opinion
484 edited by EFSA on the criteria to be used for safety evaluation of a mechanical recycling
485 process. The migration levels of the selected substances measured into the recommended food
486 simulants according standard EU conditions (10 days at 40°C) are reported in Figure 5 as the
487 percentage of the migrated additive to FSL divided by the initial quantity of the additive in
488 sample.
489 It is recognized that the release process in the packaging system is controlled by both
490 thermodynamics and kinetics, or partition and diffusion, respectively. Partition coefficient of the
491 migrant between the pure polymer and food (or FSL) at equilibrium status of the migration is
492 affected by the interaction (or affinity) of the migrant with the two phases (polymer and food
493 simulant). For the nanocomposite, the equilibrium status also depends on the additive
494 interactions with compatibilizer (in which the polar fractions alter the nature or chemical
495 properties of the nanocomposite), as well as the nanoclay which could contribute to two different
496 effects: the adsorption sites on the surface of the nanoclay could alter the partitioning of
497 additives physically, whereas the long alkyl chains of the nanoclay modifier could chemically
498 affect the additive partition coefficients. Another aspect of the additive migration from
499 nanocomposite is the kinetics (apparent diffusivity) by introducing a path tortuosity when
500 diffusing substances are forced to migrate around impermeable fillers.
501 The observed results evidenced the major influence of the nature of FSL on the migration
502 process. Regardless of the type of the molecule and sample, the additives were released almost
503 entirely to iso-octane and ethanol 95%. This is in accordance with a previous investigation on the

diffusivity of the same additives in these two simulants which were already seen to be independent of the type of the molecule (Nasiri et al., 2016). When the polymer is in contact with the fatty food simulants as iso-octane and ethanol 95%, the simulant would be able to penetrate the polymer matrix and interact with the polymer as well as the embedded nanoclay particles and act as a solvent removable penetrant. As a result, the polymer network is swelling which increases its elasticity and eventually accelerates the migration of additives. Moreover, in extreme conditions, penetration of the simulant may lead to the rearrangement of nanoclay and probable movement of nanoclay sheets within the polymer matrix. On the other hand, the interaction of the simulant with nanoclay could lead to the release of the adsorbed additives on the clay surface.

As witnessed in Figure 5, in contact with the "non-aggressive" simulants, the release of additives in nanocomposite is either equal or less than the corresponding values in the pure polymer. In these conditions, nanoclay could hinder the additive migration by slowing down diffusion through tortuous path in one hand and the adsorption of additives on the hand. Significance of the either of the effects, depends on the variety of the parameters, such as the polymer-nanoclay interaction (exfoliation, intercalation), size and steric hindrance of the diffusing molecule in addition to the nature of additives, polymer, intercalants and food simulants.

As inferred from the results of this research, for a model polymer of poor barrier properties and intrinsic non-favorable nanoclay-LLDPE interactions, and for a selection of worst-case additives, the nanocomposite of LLDPE-compatibilizer-modified nanoclay imparts no risk in terms of the exposure to interactions by-products, migration of intercalants and release of metallic elements.

Conclusion

527 This study is an attempt through a thorough analysis of the potential risks of a model
528 nanocomposite in food packaging applications by projecting the various safety aspects in a
529 model nanocomposite material, providing a database of the transfer properties of the diverse
530 components of a nanocomposite packaging in common usage conditions and introducing a
531 methodology to optimize the benefit-risk balance of their current usage as food contact materials.

532 As the wide spread application of nanocomposites in food packaging has raised concerns, more
533 studies are directed through the safety evaluation of these materials and most of these researches
534 are limited to either the extent of toxicity as a function of NP type and size or the possibility of
535 NP migration in diverse condition. This investigation presents a broader view over the
536 nanocomposite packaging safety by considering all possible interactions between the polymer,
537 nanoparticle, food, compatibilizer agent, organic modifier and the processing aids or additives
538 and demonstrates that the exhaustive study of the contact suitability of nanocomposite materials
539 is more complex than the evaluation commonly carried out for conventional materials.
540 Assessment of the interaction of nanoclay with some surrogate representatives of the packaging
541 additives or contaminants which was analysed on the basis of the relative migration of these
542 additives revealed that nanoclay tend to hinder the release of these substances in contact with
543 non-aggressive (*i.e.* aqueous) food simulants while their effect is more contrasted according to
544 the chemical nature of the migrating substance in the case of contact with a fatty simulant. The
545 role of the food simulant nature (or the affinity between polymer and food simulant) remains
546 therefore the dominant factor impacting the mass transfer properties of nanocomposite packaging
547 and, as consequence, the migration extent. In the case of low-barrier polymers such as
548 polyolefins, the migration value measured under standard conditions after 10 days of contact
549 assumes that the system is in an equilibrium state. As consequence, the transfer of additives is

mainly controlled by thermodynamic rather than kinetic factors. While nanofillers are likely to produce a tortuosity effect and thus limit the diffusion of low molecular weight molecules, their effect on the final measure of specific migration is exerted by a change in the affinity of the migrating molecules for the nanocomposite packaging. The influence of the loading rate and the spatial distribution of nanoclay are then factors that undoubtedly deserve to be investigated in any depth.

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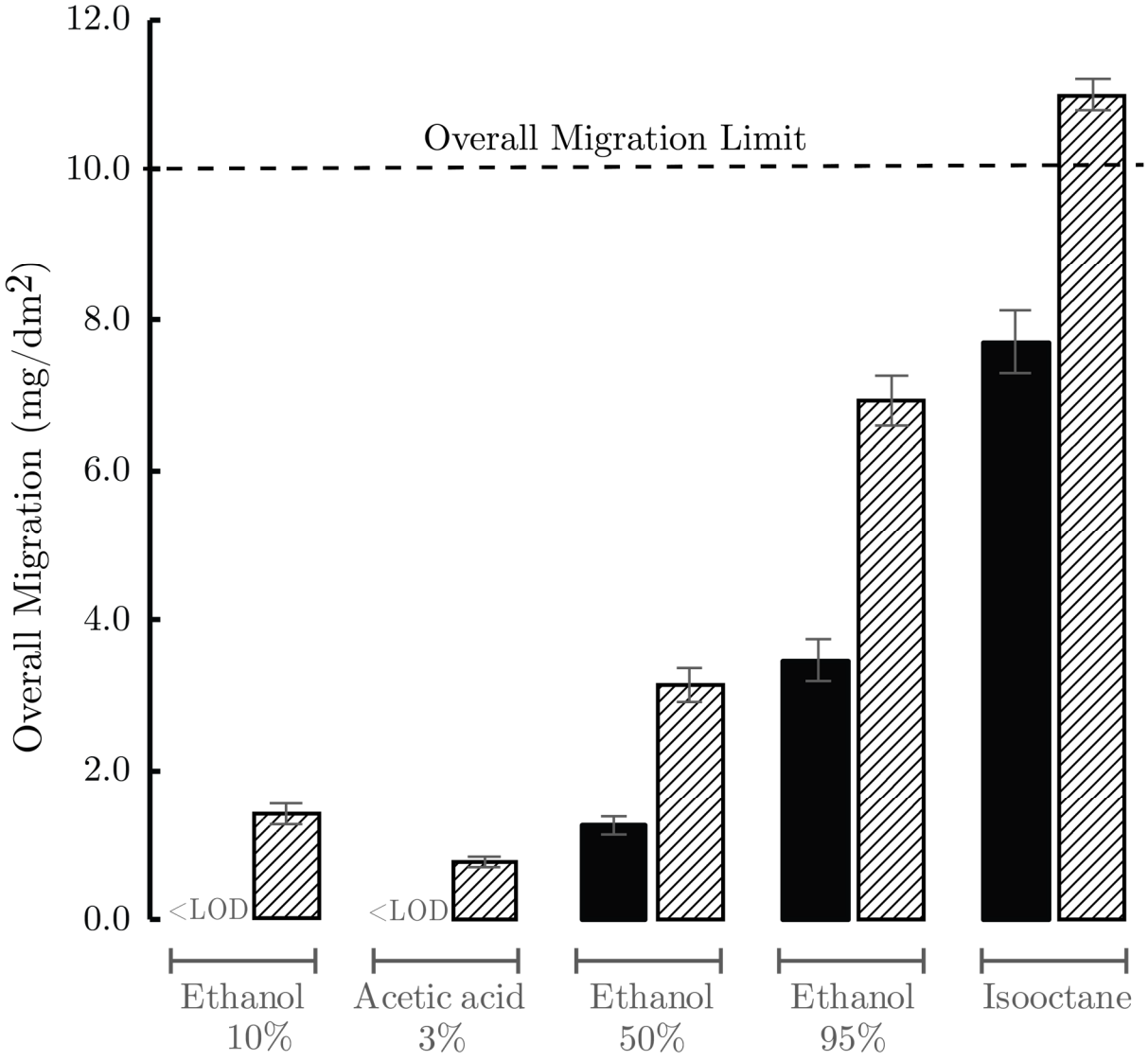


Figure 1 Comparison of the overall migration of LLDPE (■) and PNC (▨) to various food simulants (https://doi.org/10.5281/zenodo.3865149)

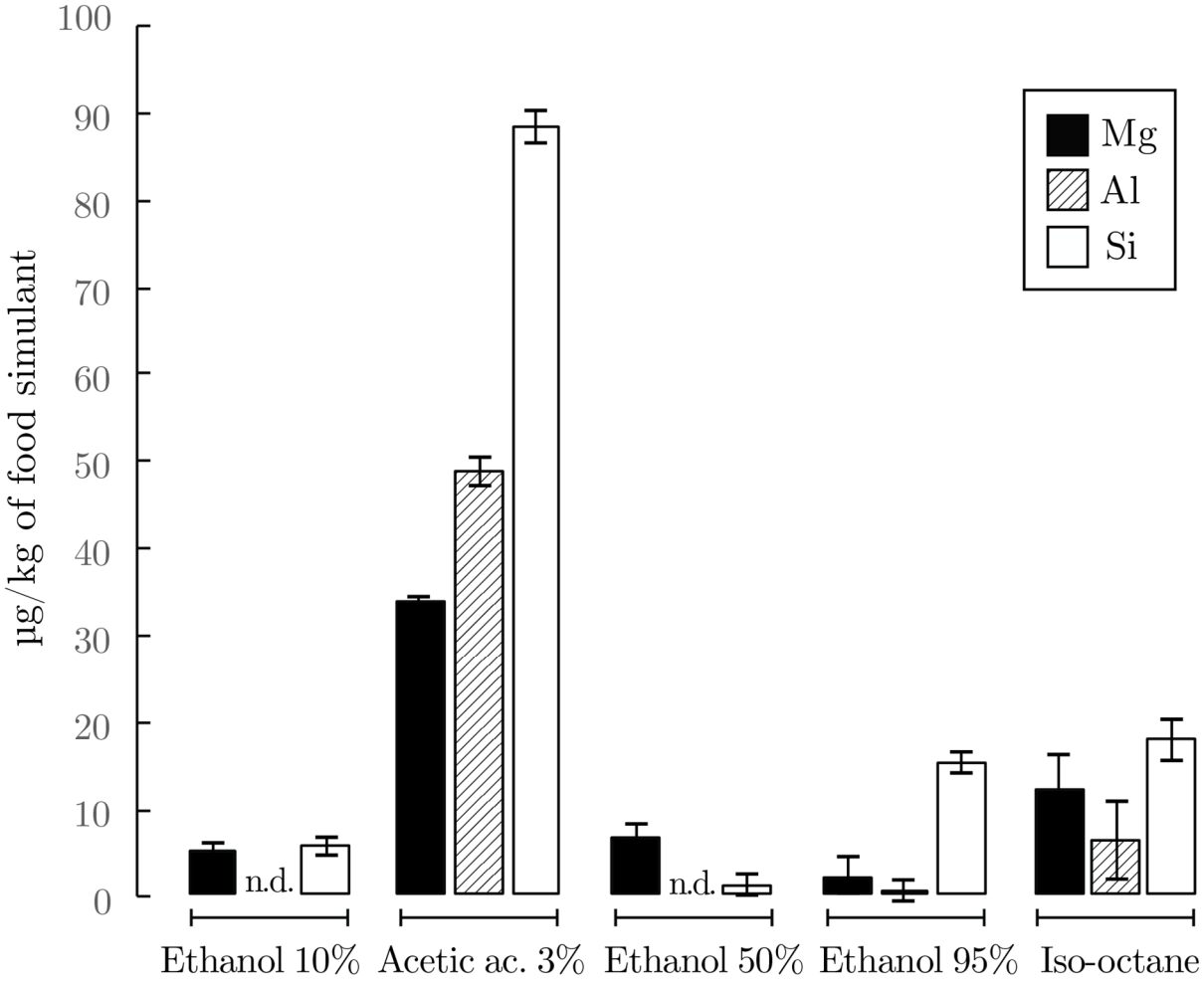


Figure 2 : Migration of Si, Al and Mg from Nanocomposite material to various food simulants (https://doi.org/10.5281/zenodo.3865149)

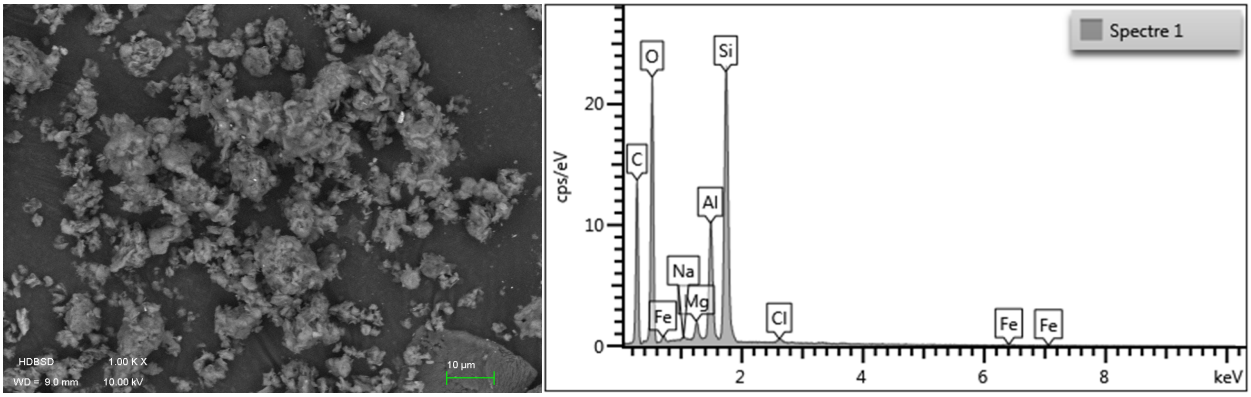
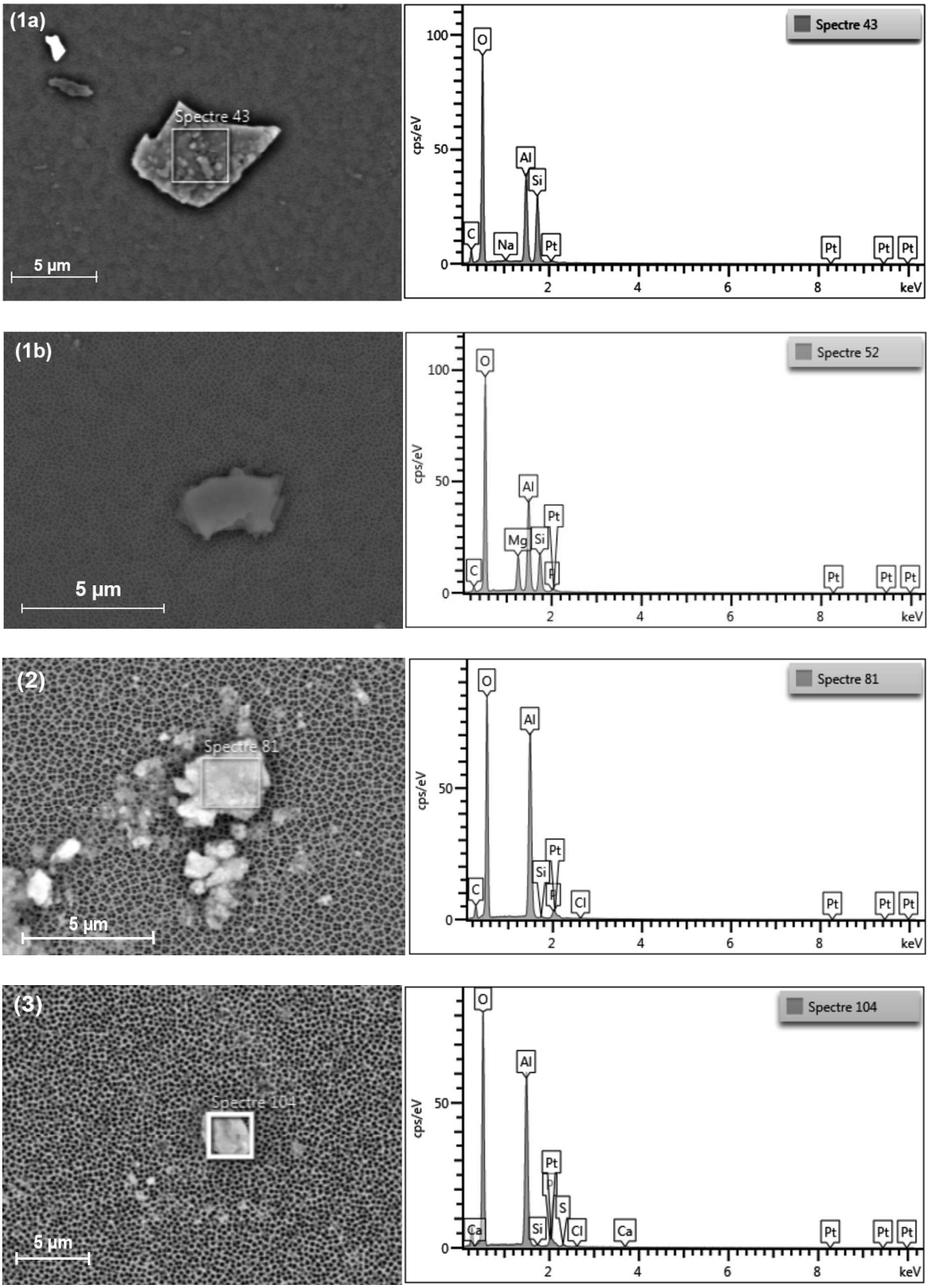


Figure 3 SEM-EDX of nanoclay powder


(1a)
Spectre 43
5 µm
Spectre 43
cps/eV
100
50
0
O
Al
Si
C
Na
Pt
Pt
Pt
Pt
2
4
6
8
keV
(1b)
5 µm
Spectre 52
cps/eV
100
50
0
O
Al
Pt
Mg
Si
C
Pt
Pt
Pt
2
4
6
8
keV
(2)
Spectre 81
5 µm
Spectre 81
cps/eV
50
0
O
Al
Pt
Si
C
Cl
Pt
Pt
Pt
2
4
6
8
keV
(3)
Spectre 104
5 µm
Spectre 104
cps/eV
50
0
O
Al
Pt
S
Ca
Si
Cl
Ca
Pt
Pt
Pt
2
4
6
8
keV

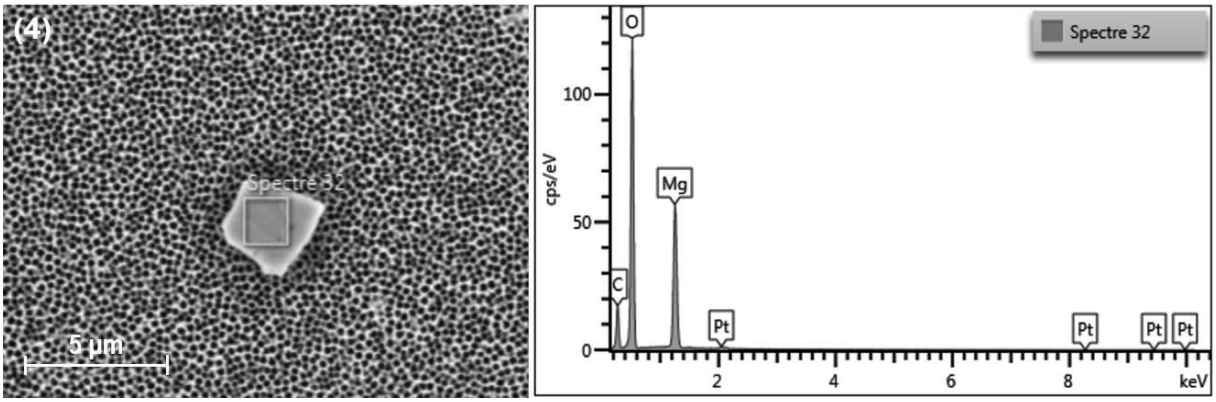


Figure 4 SEM-EDX images and corresponding spectra of filtrated particles from iso-octane (1a) and (1b); ethanol 95% (2); ethanol 50% (3) and acetic acid 3% (4).

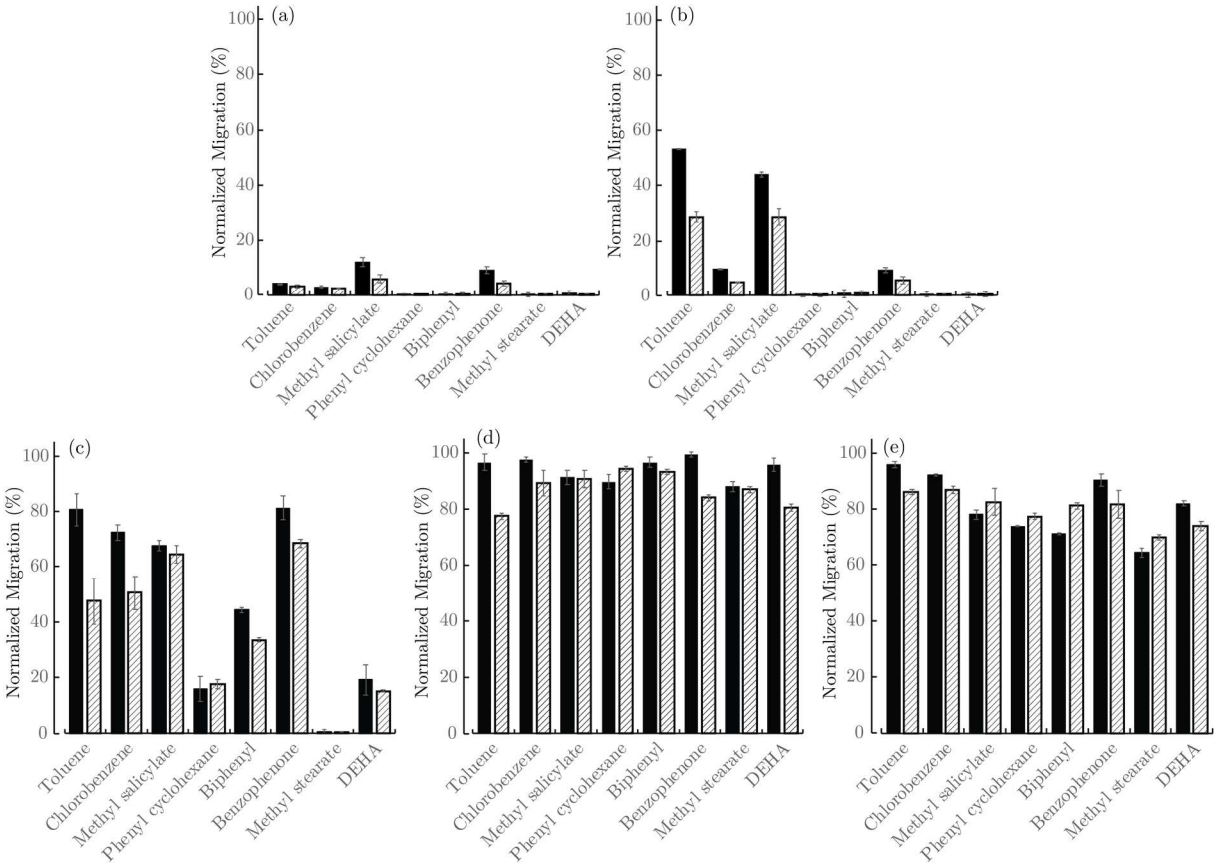


Figure 5 Normalized migration percentage of the selected additives from LLDPE (■) and PNC (▨) to Ethanol 10% (a), Acetic Acid 3 w/v% (b), Ethanol 50% (c), Ethanol 95% (d) and Iso-Octane (e) (https://doi.org/10.5281/zenodo.3865149)

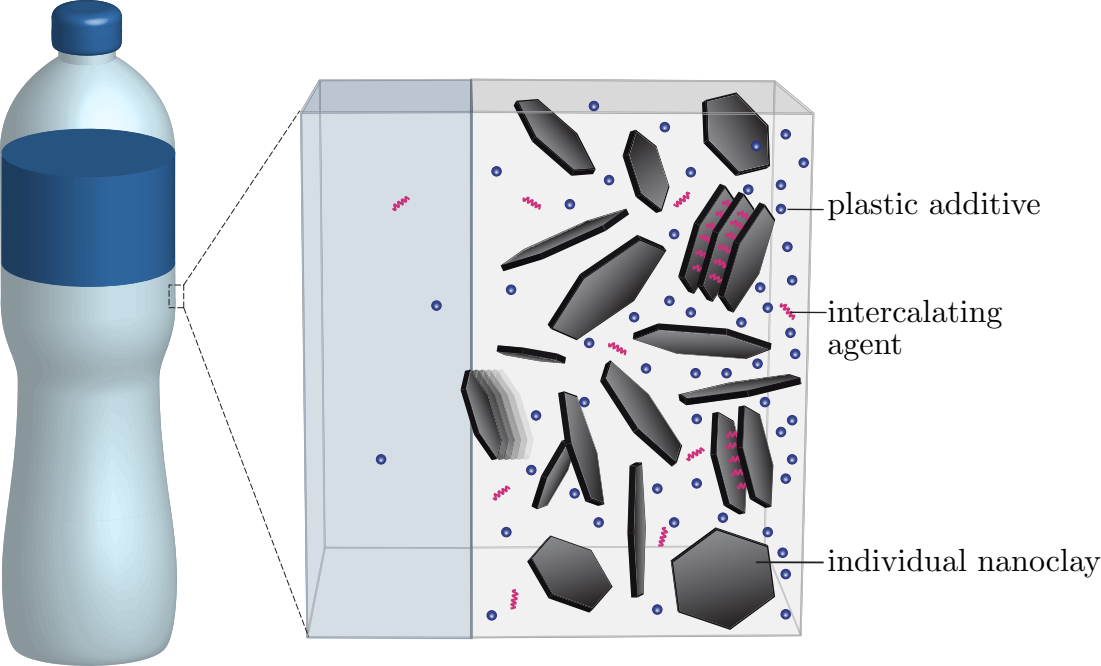
Table 1. Migration of modifier and compatibilizer from the PNC to the food simulants (mg substance per kg food simulant)

Migrant	**Food simulant**				
	Ethanol 10%	Acetic Acid 3%	Ethanol 50%	Ethanol 95%	Iso-octane
Maleic Anhydride	< LOD	< LOD	3.91 ± 0.97	8.99 ± 0.99	0.59 ± 0.16
Quaternary Alkyl Ammonium	0.01 ± 0.01	0.01 ± 0.00	0.96 ± 0.13	7.6 ± 0.15	3.35 ± 0.12

Table 2. Summary of the researches on nanoclay migration from FCMs according conventional migration testing conditions

Polymer	Food / FSL	Nanoclay type/charge	Migration Condition	Area/Vol (dm^2/L)	Migration (mg/kg)	Reference
Starch films Starch / Polyester films	lettuce & spinach	4 w/w %	40°C (10 d)	ND [a]	Si: 16 Mg :260 Si :1.3	Avella et al. 2005
Commercial 3-layer PET bottles	3% HAc	0.2 w/w % [b] Na^+-MMT	100°C (4 h)	25	None	Chaudhry et al. 2008
PLA films	95% ethanol	5 w/w % Cloisite 30B	40°C (10 d)	ND	Mg: None	Schmidt et al. 2009
Wheat gluten/nanoclay films	water 3% HAc 15% ethanol olive oil	5 w/w % Na^+-MMT	40°C (10 d)	6	Si: 1.2 (water) Si: 3.5 (3% HAc) Al: 1 (3% HAc) Si: 0.3 (15% ethanol) Si: 0.5 (olive oil)	Mauricio-Iglesias et al. 2010
PET bottles	3% HAc	3 w/w % Cloisite 20A	25°C (90 d) 45°C (90 d)	ND ASTM D-4754	Al: 0.18, Si: 6 Al: 0.34, Si: 9.5	Farhoodi et al. 2014
PLA composites	distilled water	4 w/w % MMT/HDTA 4 w/w % MT/HDTA/ACO	40°C (10 d)	8.2	Mg: 3.6 E-3 Mg:1.51 E-3	Maisanaba et al. 2014
PP/Nanocomposite/PP films	Water 3% HAc 15% EtOH olive oil grapeseed oil coconut oil	4 w/w % MMT	40°C (10 d) [c]	2	Si:0.12 Si: 1.00 Si: 0.68 Si: 1.50 Si: 1.68 Si: 1.56 Al < LOD	Huang et al. 2015
Aisaika bags (LDPE) Debbie Meyer bags (LDPE)	Ethanol 10% Acetic acid 3%	ND	40°C (10 d) [c]	16.7	Al: 0.09 Al: 0.04	Echegoyen et al. 2016

[a] Not determined (ND)
[b] Averaged over 3 layers
[c] Migration data also available for other temperature/time of contact


plastic additive
intercalating agent
individual nanoclay