



Contribution of nanoclay to the additive partitioning in polymers



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ABSTRACT

The polymer nanocomposites have become unabatedly popular due to their exceptional properties which results in a plethora of applications including the food packaging. However, safety aspect of these materials is still under debate, specifically in view point of the unknown interactions of nanoparticles with various additives added during the packages processing. For the commonly used polyolefins, the partitioning of additives rather than their diffusivity dictates the extant and extent of these interactions.

In this work, the partitioning of various additives between a clay-polymer nanocomposite (CPN) and several food simulants was measured based on a worst-case scenario in viewpoint of the selected polymer and additives. The added value of the CPN in comparison with the pure polymer (LLDPE) was analyzed with regards to their Hansen solubility parameters and log K-log P linearity. Ultimately, an estimation method based on the Flory-Huggins theory was proposed to predict the partition coefficients in CPN.

1. Introduction

The market of inorganic nanoparticle-polymer nanocomposites is rapidly growing and the packaging industry has already employed the nanotechnologies to improve the packaging properties and overall sustainability by enhancing the barrier properties, mechanical stability or by incorporating antimicrobial properties in the resulting nanocomposite. However, the market breakthrough of the polymer nanocomposites can only take place if the safety of these materials are scientifically approved. The aptitude of using polymer nanocomposites for direct food contact applications remain a controversial question due to the lack of knowledge on their migration through the packaging and as a consequence their risk to consumers' health.

From the safety point of view, the key issues in evaluating the risk of nanomaterials regarding the human exposure are: (1) the migration of the nanoparticles per se and the variables which affect their toxicity (size, shape, surface charge, solubility, aggregation) and (2) The influence of nanoparticles incorporation on the inertia of polymer nanocomposites for other (non-nano) substances into the food (Nasiri et al., 2016).

A major instance of these non-nano chemicals is the low molar mass chemical compounds (plasticizers, antioxidants, lubricants, light stabilizers and antistatic agents) which are usually incorporated within the plastic packaging to either enhance its performance and processability or to protect the package from degradation (Bhunja et al., 2013). However, the presence of nanoparticles is susceptible to modify the interactions between polymer and the additives with a possible change

in their transport properties and subsequent effect on the food contamination. Therefore, it is essential that the transport properties (i.e inertia) of polymer nanocomposite structure and the potential positive or adverse effect of the nanomaterials on these additives would be distinctively investigated from both kinetic (apparent diffusion coefficient) and thermodynamic (partition coefficient) considerations.

The migration of additives is a combination of their diffusion through the polymer, followed by the desorption of the diffusing molecules from the polymer surface to the food or food simulants (Ferrara et al., 2001). However, for low barrier polymers like polyolefins which are widely used in packaging, the diffusion coefficient could play a minor role, because the equilibrium would be reached in rather short times and long before the expiry date of the food. In this case, the main parameter influencing the migration process in these polymers is the partition coefficient ($K_{p/L}$) which is the ratio of the additive concentration in polymer to its counterpart in the food or food simulants at the equilibrium point. The values of this dimensionless variable cover many orders of magnitude, depending on the polarities, structures and sizes of the migrant, the polymer structure and the nature of food product. The exact value of $K_{p/L}$ is not known a priori and must be determined either by a time-consuming experimental or theoretical method.

In order to simplify as much as possible the theoretical treatment of migration processes from the regulatory point of view, the commonly accepted approach is to assign a KPL value of 1 recommended for "worst case scenarios" if the migrant is highly soluble in the food/food simulant or $KPL = 1000$ otherwise (Simoneau, 2010). This approxima-

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tion is not satisfactory for a more precise evaluation of product safety. Moreover, the KPL values of 1 and 1000 is facultatively applied for 'conventional' polymers but could appeared inaccurate for polymer nanocomposites.

In the specific case of low barrier polymers which quickly reach the equilibrium state after a short time of contact with food, there is a necessity for a systematic evaluation of KPL-value determination of "worst-case" additives between the nanocomposites of common packaging materials and different types of food simulants. Nevertheless, thus far only few solid/liquid partition coefficient values of some chemical substances in nanocomposites have been reported in literature (de Abreu et al., 2010; Rodríguez et al., 2014).

The present study is focused on the comparison of the partition coefficient of low- and medium-molar mass substances in a nanocomposite versus the pure polymer in contact with various simulants which represent different types of food. To explore a worst case migration scenario, polyethylene, the most commonly used polymer in the packaging industry, was chosen as the matrix which exhibits low barrier properties organic compounds. Organo-modified nanoclay was used as the filler for clay-polymer nanocomposites (CPN) because of its proven efficiency in barrier properties due to their high aspect ratios (Azeredo, 2009; Patel et al., 2006).

The experiments were conducted according to a Challenge Test in line with the recommendations of the Food and Drug Administration (FDA) and European Food Safety Authority (EFSA) for determining the decontamination efficiency of the recycling process for recycled polymer packaging (EFSA, 2011; Food and Administration, August 2006). In consequence, several model additives, representative of the additives introduced in the packaging processing, were selected and their partition coefficients in CPN as well as the neat polymer were measured. In an attempt to conduct a more rational approach for explaining CPN-solute partition coefficient values, properties such as the solute octanol-water partitioning coefficient (Log P) and polymer-additive Hansen solubility distances have been considered. Moreover, since the measurement of contaminants partition coefficients in every plastic packaging is cumbersome, it was tried to assess the log K-log P behavior and to predict the K-values based on the activity coefficients. The aim of such approach is also to further progress in the understanding of mechanisms which control the partitioning in food packaging system involving nanomaterials.

2. Material & methods

2.1. Chemicals and food simulants

Selection of solid and liquid surrogates, was based on FDA and EFSA regulations so that they would be representatives of all general categories of chemicals such as volatile and non-polar, volatile and polar, non-volatile and polar and non-volatile and non-polar (EFSA, 2011; Food and Administration, August 2006). The solid additives (biphenyl, benzophenone and methyl stearate) and liquid contaminants (toluene, chlorobenzene, methyl salicylate, phenyl cyclohexane and DEHA) were all provided by Sigma-Aldrich with high purity.

Linear low density polyethylene (LLDPE, LL 1002YB melt flow index 2.0 g/10 min, density 0.918 g/cm³), supplied by Exxon Mobil Chemical, was chosen as the polymer matrix. Cloisite 20 (C20), a Bis (hydrogenated tallow alkyl)dimethyl ammonium bentonite salt, was provided by BYK Additives & Instruments. Fusabond E226 (DuPont™), a maleic anhydride modified polyethylene (MA-g-PE) with melt flow index of 1.75 g/10 min and density of 0.93 g/cm³, was chosen as a compatibilizer between nanoclay and the base polymer.

Five food simulant liquid (FSL) were used according to the EU regulation 10/2011 to assess the partition coefficients of additives between the polymer samples and FSLs (Commission, 2011). The selected food simulants encompass 3 w/v% aqueous acetic acid to represent acidic food, ethanol 10% to simulate aqueous food, ethanol

50% for alcoholic foods (with alcohol content of > 20%) as well as the dairy products and ethanol 95% and isooctane which are both representing fatty foods.

2.2. Clay-polymer nanocomposite processing

The clay-polymer nanocomposite was synthesized with LLDPE, 5 wt % of C20 and 15 wt% of MA-g-PE by melt intercalation method using a co-rotating twin screw extruder (Thermo Scientific™ EuroLab 16) with a L/D ratio of 40 and a screw diameter of 16 mm at screw speed of 200 rpm and feed rate of 1.0 kg/h (Nasiri et al., 2016). The control sample of pure LLDPE was also undergone the same thermal processes as the CPN.

2.3. Impregnation of CPN & Migration tests

The virgin polymer and CPN were contaminated with 500–1000 ppm of each additive as recommended by EFSA (EFSA, 2011). Once the contaminants were thoroughly mixed with the samples, they were stored at 40 °C under rotary agitation. After one week, the CPN pellets were rinsed with distilled water and divided to be subjected to the five food simulants.

According to the previously determined contact time which was obtained on the basis of desorption kinetics in order to ensure an equilibrium state, desorption test was performed at 40 °C for two weeks with periodic agitation. By the end of the period, aliquots of each simulant were collected to be analyzed by gas chromatography (GC-FID, Agilent 7890A gas chromatograph equipped with a HP-5 capillary column of 32 mm × 30 m × 0.25 μm) to determine the equilibrium concentration of each additive in the simulants. The samples were also extracted with pure dichloromethane (DCM) to obtain equilibrium concentration of additives in polymer samples after the desorption process (C_p).

Beware of the volatility of some additives, another experiment was performed to monitor the analyte loss in the food simulants at the same conditions of time and temperature and subsequently the correction factors were exerted to correct for the loss of chemical additives in headspace.

2.4. Structural characterization

The degree of exfoliation of the tested CPN was examined by X-ray Diffraction method. X-ray diffraction (XRD) measurements were performed with a PANalytical X'Pert diffractometer with the Cu K_α radiation (λ = 1.54 Å) in the reflection mode. The results were indicated that the C20 characteristic reflection at 2θ of 2.56 has disappeared for the CPN which is due to the exfoliation of nanoclays layers in the polymer nanocomposite. The same measurements were also applied over a 2θ range of 16–26° on pure LLDPE and CPN before and after the 10-days contact with Ethanol 95% and isooctane in order to assess the crystallinity of the samples. The XRD patterns and further information on the CPN structure (e.g. TEM micrographs) could be found in the recent study (Nasiri et al., 2016).

2.5. Determination of partition coefficient

Experimental partition coefficient values were calculated between liquid and polymer phase as the ratio of the equilibrium concentration of the solute in polymer sample to its compartment in food simulant. While the latter concentration is directly measured in GC-FID, the former is obtained from the solute concentration in the extracting solvent, DCM, and the partition coefficient (K_{p/f}) was calculated as:

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