

Migration of engineered nanoparticles from polymer packaging to food – a physicochemical view

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Summary

A physicochemical perspective on the potential migration of engineered nanoparticles (ENPs) from packaging to food is presented, based on evaluation of the average distance travelled by ENPs in the polymer matrix. The study has taken into account physicochemical properties of both ENPs and packaging polymers. From the properties, some general characteristics underpinning ENP migration can be predicted. The results indicate that any detectable migration of ENPs from packaging to food will take place in the case of very small ENPs with a radius in the order of 1 nm, from polymer matrices that have a relatively low dynamic viscosity, and that do not interact with the ENPs. These conditions are likely to be met in the case of nanocomposites of silver with polyolefines (LDPE, HDPE, PP). It can also be predicted that there will not be any appreciable migration in the case of bigger ENPs, that are bound in polymer matrices with a relatively high dynamic viscosity such as polystyrene and polyethylene terephthalate.

Keywords:

engineered nanoparticle; nanomaterial; migration; diffusion; food; packaging; food contact material

Foodstuffs need appropriate packaging to maintain quality and freshness during transportation and storage, and to extend shelf life by controlling the movement of moisture, gases (oxygen, carbon dioxide) and certain volatile components such as flavours. Requirements for food packaging have changed over the years with an increasing demand for packaging materials that are stronger but lightweight, biodegradable or recyclable, and have certain functional properties. The labels on food packaging are also expected to provide a means for monitoring the quality, safety, security and traceability of food products in the supply chain. The advent of nanotechnology, which involves manipulation of materials in the particle size range of up to 100 nanometres (nm) in one or more dimensions, has opened up new opportunities for the development of innovative packaging materials that can address many of the industry needs. Nanotechnology has started to make an impact on the global food and associated sectors, although many of the applications for food and beverages are currently at research and development or near-mar-

ket stages [1]. Compared to this, applications for food packaging are rapidly becoming a commercial reality and already make up the largest share of the current and short-term predicted nanofood market [2].

The incorporation of engineered nanoparticles (ENPs) in food packaging materials leads to several benefits. Due to the extremely small size, ENPs have a very large reactive surface area on an equivalent weight basis compared to conventional bulk materials. Thus unlike conventional fillers and additives, much lower amounts of ENPs are usually sufficient to improve the properties of packaging materials without any significant change in density, transparency or processing characteristics [3]. The ENP-polymer composites (also termed as nanocomposites) are typically reinforced with up to 5% (w/w) of ENPs and this can bring a drastic improvement in the properties and performance of the polymer. For example, incorporation of certain ENPs into plastic polymers has been reported to render them light, fire resistant [4], stronger in terms of mechanical and thermal characteristics

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[5–7], and provide an effective barrier against diffusion of gases [6, 8]. The incorporation of certain metal and metal-oxide ENPs in polymers has also led to the development of ‘active’ packaging materials that prevent growth of microorganisms and hence preserve quality of foods during transportation and storage. The polymers used for the development of nanocomposites are polyamides (PA), nylons, polyolefins, polystyrene (PS), ethylene-vinylacetate (EVA) copolymer, epoxy resins, polyurethane, polyimides and polyethyleneterephthalate (PET) [9].

A number of nanotechnology-derived food packaging materials are already available in some countries, albeit largely outside the EU. It is, however, widely expected that they will be increasingly available in the EU in the coming years. A recent review [1] has identified the following broad categories of nanocomposite-based food contact materials (FCMs):

- Improved FCMs incorporating ENPs for better packaging properties in terms of flexibility, durability and temperature or moisture stability. Typical examples include polymer composites with nanoclay (for an improved gas barrier), nano-silicon dioxide (for abrasion resistance), titanium dioxide (for UV protection) and titanium nitride (as a processing aid or for mechanical strength). Nanoclay-polymer composites are among the first nanocomposites to emerge on the market as improved packaging materials. The nanoclay mineral used in these nanocomposites is montmorillonite, which is commonly obtained from volcanic ash or rocks. Nanoclay has a natural nano-scaled layer structure, which, when incorporated in a polymer, restricts the permeation of gases. Substantial improvements in gas barrier properties of polymer composites containing nanoclay have been claimed [10]. Potential uses of nanoclay-polymer composites have been suggested for a variety of food packaging applications, for example processed meats, cheese, confectionery, cereals, boil-in-the-bag foods, and in extrusion-coating applications for fruit juices and dairy products, or co-extrusion processes for the manufacture of bottles for beer and carbonated drinks [11]. Examples of the available nanoclay-polymer composites with Nylon-6 include: Imperm®, Duretham® LDPU 601 and Aegis® OX. A few Breweries have been reported to be already using the technology in their beer bottles [1].
- ‘Active’ FCMs incorporating metal or metal oxide ENPs (e.g. silver, zinc oxide, magnesium oxide) for antimicrobial properties. Examples

include polymer composites with nanosilver, claimed to preserve the food within the packaging materials longer by inhibiting the growth of microorganisms. The recent discovery of the antimicrobial properties of ENPs of zinc oxide and magnesium oxide [12] is hoped to enable their use as a more affordable food packaging solution. Nano-zinc oxide based films for wrapping foodstuffs are already available commercially [13].

- ‘Intelligent’ and ‘Smart’ food packaging incorporating nanosensors to monitor the condition of the food during transportation and storage. Of particular interest are nanotechnology-derived food safety and quality indicators that can be applied as labels or coatings and which add an intelligent function to food packaging in terms of ensuring the integrity of the package by detecting leaks (for foodstuffs packed under vacuum or inert atmosphere), time-temperature variations (e.g. freeze-thawing) or microbial safety (deterioration of foodstuffs). One example is an oxygen detecting ink containing light-sensitive (TiO_2) ENPs, which only detect oxygen when they are ‘switched on’ with UV light [14]. Another example of food quality indicator is a label based on hydrogen sulphide detection, which is designed for use with fresh poultry. The indicator is based on a reaction between hydrogen sulphide and nano-layer of silver, which is opaque light brown. If meat starts to deteriorate silver sulphide is formed and the layer become transparent [15].
- Biodegradable polymer-nanomaterial composites. This is an emerging area of research and development where incorporation of certain ENPs has been found to improve the properties of biodegradable polymers. Examples include nanoclay composites with starch or polylactic acid polymers that have much improved mechanical and moisture barrier properties compared to polymers alone [6, 11].

Despite the potential of nanotechnology to revolutionize the food sector from production to processing, packaging, transportation and storage, such applications have also raised a number of consumer safety, environmental, ethical, policy and regulatory issues. The main concerns stem from the lack of knowledge over the potential effects of ENPs on human health and the environment. This is because physicochemical and biological properties of materials at nano-size can be substantially different from conventional bulk forms, and their effects and impacts may not be accurately predicted from the existing knowledge

derived from conventional bulk materials. There have already been calls for a moratorium [16, 17] or an outright ban [18] on the technology until it is proven to be safe.

There is a growing body of scientific evidence, which indicates that some free ENPs may cause harm to biological systems because of their ability to penetrate cellular barriers [19] and induce oxygen radical generation that may cause oxidative damage to the cell [20–23]. However, toxicological studies on ENPs in relation to gastrointestinal intake are sparse and the available information largely relates to exposure through inhalation route. Thus, the nature and extent of risks to consumer health from ingestion of ENPs via food and drinks are currently unknown. Also, despite the claimed antimicrobial effects of certain ENPs, there is currently no published research on their likely effects on the gastrointestinal tract or the natural gut microflora when ingested via food or drinks.

The likelihood of consumer exposure from consumption of foodstuffs packaged in materials made of nanocomposites is, however, dependent on the migration of ENPs into food and drinks. The experimental data on migration of ENPs from FCMs are virtually not available. Currently, there is only one published study [24] that has determined migration of minerals from biodegradable starch and nanoclay nanocomposite films. This experimental work involved putting vegetable samples (lettuce and spinach) into bags made of either potato starch or potato starch-polyester blend and their respective composites with nanoclay. The bags were heated at 40 °C for 10 days, cooled, acclimatized and migration of minerals determined by an atomic absorption method after digestion of the vegetables. The results of the tests indicated an insignificant trend in the levels of Fe and Mg in the vegetables, but a slight increase in the amount of Si, which is the main component of the nanoclay (16–19 mg.kg⁻¹ Si in vegetables packaged in nanoclay-composites with potato starch and potato starch-polyester blend, 13 mg.kg⁻¹ in the same polymers without nanoclay and around 3 mg.kg⁻¹ in neat vegetables). This study, however, only provides a small piece of information in relation to a biodegradable material and not to other plastic polymers that are commonly used for FCMs, such as PET, PE or PP. The lack of migration data currently poses a major stumbling block to the assessment of risks to an average consumer from the consumption of foodstuffs packaged in nanocomposite-based materials. Another difficulty relates to the limited number of methods (e.g. atomic absorption, ICP-MS) that are available for the de-

tection and quantification of ENPs. Also, current analytical methods are not sensitive enough to enable determination of size distribution, shape and form of ENPs, in particular when they are in very low concentrations or are in a complex food matrix [25, 26]. In view of these difficulties and to fill the current knowledge gaps, this article is aimed at assessing the potential rate of migration and the equilibrium distribution of ENPs from food packaging materials on the basis of physicochemical considerations.

THERMODYNAMIC ASPECTS

Theoretically, the migration of ENPs from a nanocomposite-based packaging to food will take place until an equilibrium distribution of ENPs between the packaging and food is established. A prerequisite for the equilibrium distribution of ENPs is the equality of the chemical potentials of ENPs in food (μ_f) and the polymer (μ_p) [27]:

$$\mu_f = \mu_p \quad (1)$$

After expressing the chemical potentials via the terms of the standard chemical potentials and activities, one can get:

$$\mu_f^\ominus + RT \ln a_f = \mu_p^\ominus + RT \ln a_p \quad (2)$$

where μ_f^\ominus and μ_p^\ominus are the standard chemical potentials of the ENPs in food and in the polymer, respectively, a_f and a_p are the activities of ENPs in food and the polymer, R is the gas constant and T stands for the absolute temperature. The distribution coefficient of the ENPs between food and the polymer, K , can be expressed from Eq. (2):

$$K = \frac{a_f}{a_p} = \exp \left[\frac{\mu_p^\ominus - \mu_f^\ominus}{RT} \right] \quad (3)$$

The concentration of migrating ENPs both in the polymer and food is assumed to be small. Thus, the ENPs interact predominantly with the surrounding matrix and the standard chemical potentials reflect the strength of interactions between the ENP and the polymer or food. The stronger the interaction, the more negative is the standard chemical potential. For example, if the interaction between ENP and the polymer is stronger than the interaction between ENP and food, then the argument in the exponential function of Eq. (3) becomes negative and the distribution coefficient is $K < 1$. In this case, the activity of ENPs in food will be lower than that in the polymer.

The activities can be expressed as a product of activity coefficient and concentration [27]. Adopt-

ing the frequently used approximation that the activity coefficients are equal to one, the activities can be replaced by concentrations. Hence, Eq. (3) can be rewritten as

$$K \approx \frac{c_f}{c_p} = \frac{N_f}{N_p} = \exp \left[\frac{\mu_p^\ominus - \mu_f^\ominus}{RT} \right] \quad (4)$$

where c_f and c_p are the equilibrium concentrations of ENPs in food and in the polymer, respectively, and N_f and N_p are the equilibrium numbers of ENPs in the volume unit of food and the polymer, respectively.

The equilibrium distribution of ENPs between food and the polymer expressed by Eq. (4) is not established immediately, the migration of ENPs takes some time. The difference between the actual concentrations of ENPs and those given by Eq. (4) is a driving force for the ENPs to migrate.

RATE OF MIGRATION (DIFFUSION)

Diffusion is the migration of matter down a concentration gradient. The rate of diffusion is described by the diffusion equation, also called Fick's second law of diffusion, which relates the rate of change of concentration at a point to the spatial variation of the concentration at that point. The diffusion coefficient, D , occurring in the Fick laws, represents a measure of the rate of molecular motion and can be calculated by the Stokes-Einstein relation [27]:

$$D = \frac{k_B T}{6\pi\eta a} \quad (5)$$

where k_B is the Boltzmann constant ($k_B = 1.3807 \times 10^{-23} \text{ J.K}^{-1}$), a is the particle radius and η is the dynamic viscosity of the fluid. In this case, the amorphous polymer matrix is understood a fluid. The solutions of the diffusion equation can be used to calculate the net distance through which the particles diffuse in a given time. The average distance, r , travelled by particles is [27]

$$r = 2 \left(\frac{Dt}{\pi} \right)^{1/2} = \left(\frac{2k_B T t}{3\pi^2 \eta a} \right)^{1/2} \quad (6)$$

where t is the migration time.

If the packaging is not in the contact with food, the ENPs are distributed evenly within the polymer matrix. Another aspect is that as ENPs move in all directions and they are reflected back to the polymer bulk when reaching the packaging wall. In this way, the ENPs migrate within the polymer matrix

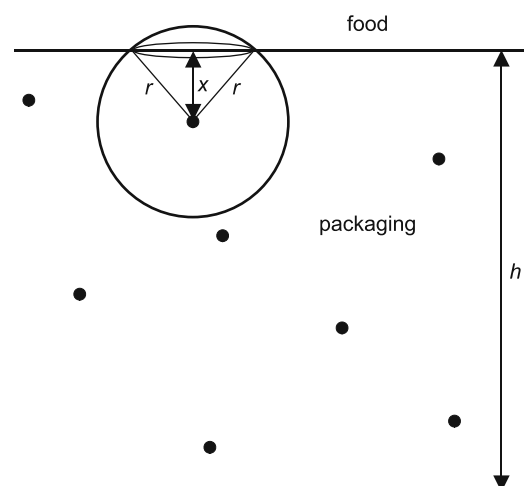


Fig. 1. Illustration of the migration of nanoparticles from packaging to food.

but their concentration remains unchanged. After contacting the packaging with food, the ENPs may not be reflected at the packaging wall and they may enter the food matrix. For the sake of simplicity, we assume that the interphase boundary between the polymer and food does not represent any obstacle for the movement of ENPs so that each ENP impinging on the packaging wall will enter the food matrix.

The migration of ENPs after contacting the packaging and food is illustrated in Fig. 1; the small black circles depict the ENPs. The ENPs move in all directions so that the conceivable positions of a migrating ENP at time t form a sphere. As seen from Fig. 1, only those ENPs can enter the food matrix, which are not further from the packaging wall than the average migration distance. The possible positions of an ENP entering the food matrix form a spherical cap, i.e. the region of the sphere which lies above the plane given by the packaging wall. The surface of the spherical cap is given as

$$S_c = 2\pi r v \quad (7)$$

The height of the cap, v , can be expressed as

$$v = r - x \quad (8)$$

where x is the distance of ENP from the packaging wall. The surface of the sphere is given by the relationship

$$S_s = 4\pi r^2 \quad (9)$$

As reasoned above, the condition for the migration of ENP from packaging to food is $x \leq r$ so that the probability of migration of ENP with the distance x from the packaging wall to food is S_c/S_s . Taking into account Eqs. (7)–(9), the aver-

age probability of ENP migration from packaging to food from the region $x \leq r$ can be expressed as

$$q = \frac{1}{r} \int_0^r \frac{S_c}{S_s} dx = \frac{1}{r} \int_0^r \frac{r-x}{2r} dx = \frac{1}{4} \quad (10)$$

As follows from Eq. (10), only a quarter of ENPs from the region $x \leq r$ leave the packaging and enter the food matrix. Amount of the ENPs migrating from the packaging to food during time t , n , can be expressed as

$$n = qrSc_0 \quad (11)$$

where S is the surface of the packaging and c_0 is the initial concentration of ENPs in the packaging. The ability of ENPs to migrate from the packaging to food, i.e. the migratability (m), can be defined as

$$m = qr = \frac{n}{Sc_0} = \frac{1}{4} \left(\frac{2k_B T t}{3\pi^2 \eta a} \right)^{1/2} = \left(\frac{k_B T t}{24\pi^2 \eta a} \right)^{1/2} \quad (12)$$

The migratability means the amount of ENPs migrating from packaging to food through a unit of packaging surface assuming a unit initial concentration of the ENPs in the packaging. The value of migratability does not depend on the dimension of concentration. The dimension of concentration can be $\text{mol} \cdot \text{m}^{-3}$, number of ENPs in 1 m^3 or $\text{kg} \cdot \text{m}^{-3}$. Then, the amount of ENPs is expressed in corresponding units (mol, number of particles or kg).

It follows from Eqs. (11) and (12) that the amount of ENPs migrating from packaging to food can be evaluated very simply by the relationship

$$n = mSc_0 \quad (13)$$

RESULTS AND DISCUSSION

As seen from Eqs. (5), (6) and (12), for the estimation of the migration of ENPs from packaging to food, the value of polymer dynamic viscosity at the temperatures of food storage are needed. In

literature, the data for polymer melts are available. To obtain the viscosity of the polymers at the food storage temperature from the melt viscosity, it is necessary to assess the temperature dependence of the viscosity. We used the Williams-Landel-Ferry equation which is often used for polymer melts or other fluids that have a glass transition temperature. The equation is [28]:

$$\eta(T) = \eta(T_g) \exp \left[-\frac{C_1 (T - T_g)}{C_2 + T - T_g} \right] \quad (14)$$

where C_1 and C_2 are empirical parameters, T_g is the glass transition temperature and $\eta(T_g)$ is the viscosity at the glass transition temperature. The parameters C_1 and C_2 are very similar for the wide class of polymers and their values are $C_1 = 17.44$ K and $C_2 = 51.6$ K.

The values of viscosities of polymer melts encountered in literature are quite scattered and very often differ by more than an order of magnitude. We used the values of polymer melt viscosities from references [29–31], the values of glass temperatures were taken from [32]. For low-density polyethylene (LDPE), high-density polyethylene (HDPE) and polypropylene (PP), the viscosities for temperatures 25 °C, 4 °C and –18 °C, corresponding to the ambient, refrigerator and freezer food storage temperatures, were calculated. It is meaningless to use Eq. (13) for temperatures below T_g . For polystyrene (PS) and polyethylene-terephthalate (PET), the values of T_g are higher than the selected storage temperatures. Since viscosity tends to increase as temperature decreases, the viscosities of these polymers were assessed to be lower than those at T_g . The viscosities are listed in Tab. 1. The values of dynamic viscosity of polymers increases in the order LDPE < HDPE < PP < PET < PS.

In Tab. 2, the values of diffusion coefficients for ENP with the radius of 5 nm are listed. This radius was chosen since it is typical for many engineered nanoparticles. For comparison, diffusion

Tab. 1. Dynamic viscosities (η) of polymer melts, glass transition temperatures (T_g) and recalculated viscosities for various storage temperatures.

Polymer	η [Pa.s]	Reference	T_g [°C]	η [Pa.s] 25 °C	η [Pa.s] 4 °C	η [Pa.s] –18 °C
LDPE	8000 at 150 °C	29	–100	6.6×10^4	1.3×10^5	2.1×10^5
HDPE	5000 at 190 °C	29	–70	1.3×10^5	3.6×10^5	1.6×10^6
PP	2400 at 190 °C	30	–30	4.1×10^5	3.2×10^6	1.2×10^8
PET	1000 at 285 °C	31	69	$> 1 \times 10^9$	$> 1 \times 10^9$	$> 1 \times 10^9$
PS	3×10^4 at 190 °C	29	95	$> 2 \times 10^9$	$> 2 \times 10^9$	$> 2 \times 10^9$

Tab. 2. Diffusion coefficients (D) for ENP with a radius of 5 nm in various polymer matrices and various temperatures.

Polymer	D [$\text{m}^2\cdot\text{s}^{-1}$] 25 °C	D [$\text{m}^2\cdot\text{s}^{-1}$] 4 °C	D [$\text{m}^2\cdot\text{s}^{-1}$] –18 °C	$D(\text{CO}_2)$ [$\text{m}^2\cdot\text{s}^{-1}$] 25 °C
LDPE	6.62×10^{-19}	3.12×10^{-19}	1.78×10^{-19}	3.72×10^{-11}
HDPE	3.36×10^{-19}	1.13×10^{-19}	2.34×10^{-20}	1.24×10^{-11}
PP	1.07×10^{-19}	1.27×10^{-20}	3.12×10^{-22}	–
PET	$< 4.37 \times 10^{-23}$	$< 4.06 \times 10^{-23}$	$< 3.74 \times 10^{-23}$	5.4×10^{-14}
PS	$< 2.18 \times 10^{-23}$	$< 2.03 \times 10^{-23}$	$< 1.87 \times 10^{-23}$	5.8×10^{-12}

For comparison, diffusion coefficients of CO_2 are included.

Tab. 3. Migratabilities (m) of ENPs with a radius of 5 nm for various storage temperatures and various polymer matrices.

Polymer	m [m] 25 °C 1 month	m [m] 25 °C 1 year	m [m] 4 °C 1 month	m [m] 4 °C 1 year	m [m] –18 °C 1 month	m [m] –18 °C 1 year
LDPE	3.7×10^{-7}	1.3×10^{-6}	2.5×10^{-7}	8.9×10^{-7}	1.9×10^{-7}	6.7×10^{-7}
HDPE	2.6×10^{-7}	9.2×10^{-7}	1.5×10^{-7}	5.3×10^{-7}	6.9×10^{-8}	2.4×10^{-7}
PP	1.5×10^{-7}	5.2×10^{-7}	5.1×10^{-8}	1.8×10^{-7}	8.0×10^{-9}	2.8×10^{-8}
PET	$< 3.0 \times 10^{-9}$	$< 1.0 \times 10^{-8}$	$< 2.9 \times 10^{-9}$	$< 1.0 \times 10^{-8}$	$< 2.8 \times 10^{-9}$	$< 9.7 \times 10^{-9}$
PS	$< 2.1 \times 10^{-9}$	$< 7.4 \times 10^{-9}$	$< 2.0 \times 10^{-9}$	$< 7.1 \times 10^{-9}$	$< 2.0 \times 10^{-9}$	$< 6.8 \times 10^{-9}$

coefficients of a relatively bulky molecule, i.e. CO_2 [33], were also included in Tab. 2. It can be seen that the diffusion coefficients of ENP are by 8–11 orders of magnitude lower than the diffusion coefficients of CO_2 . This indicates that the diffusion of nanoparticles in polymers is very slow.

As seen from Eq. (12), the migratability depends on many variables. First, it depends on the square root of time. The other variable is temperature where the dependence is not so straightforward as in the case of time. Temperature occurs explicitly in Eq. (12) in the numerator of the fraction. However, it occurs also implicitly in the denominator in the value of dynamic viscosity which depends on temperature as shown in Eq. (14). Hence, migratability increases with increasing temperature. The last variable affecting the migratability is the radius of ENP. If ENP does not interact with the polymer matrix, it can be assumed that the radius equals that determined for pristine ENP. Any interaction with the polymer matrix slows down the movement of ENP. The migrating ENP has to “drag” the interacting macromolecules so that its effective radius may increase by several orders of magnitude with a subsequent decrease in the value of migratability.

Tab. 3 summarizes the migratabilities of ENPs with the radius of 5 nm for various storage tem-

peratures and various polymer matrices. From the values of migratabilities, the amount of migrating ENPs can be estimated using Eq. (13). For example, the value of migratability for LDPE at 25 °C over one year of contact between packaging and food is 1.3×10^{-6} m. Provided that the initial concentration of silver ENPs in the packaging is $c_0 = 1 \text{ kg}\cdot\text{m}^{-3}$ (i.e. $1 \text{ g}\cdot\text{dm}^{-3}$) and the packaging surface is $S = 0.2 \text{ m}^2$, then $n = 2.6 \times 10^{-7}$ kg of nanosilver (0.26 mg) will migrate from packaging to food during the 1 year contact between food and packaging. For PET, the value of migratability is $m < 1.1 \times 10^{-9}$ m, which means that less than 2.2×10^{-10} kg (0.22 μg) of nanosilver will migrate from packaging to food during one year at 25 °C. These examples indicate that any significant migration of ENPs from packaging to food can be expected solely in the case of very small ENPs (with the radius in the order of 1 nm) from the polymer matrices with relatively low dynamic viscosity, and which also do not interact with the ENPs. Migration of nanosilver from polyolefines (LDPE, HDPE, PP) fulfills these requirements. For bigger ENPs bound in polymer matrices with a relatively high dynamic viscosity, the migration is not likely to be detectable. This corresponds to nanosilver incorporated in PET and PS, or montmorillonite with surface modification embedded in various po-

lymer matrices.

It is necessary to stress that the estimation of migratability by Eq. (12) represents its highest limit and is almost surely overestimated. This is based on an assumption that the interphase boundary between the polymer and food does not represent any obstacle for the movement of ENPs. This may not be true in all cases, and some ENPs may be reflected back to the polymer matrix at the interphase boundary. Another, a less important reason for the overestimation of the migratability, is the implicit assumption in Eqs. (11)–(13) that the concentration of ENPs is constant and equals c_0 and does not change as the ENPs migrate to food matrix. In fact, the concentration should decrease as the ENPs migrate to food. As the examples in the above paragraph show, even the overestimated assessment shows that the migration of ENPs from packaging to food can be negligible for standard storage times and temperatures.

Eq. (4) shows that an equilibrium between the concentration of ENPs in packaging and food should be established after a sufficiently long time. The equilibrium is expressed by the distribution coefficient K . Let us estimate the time needed for establishing the equilibrium. For example, the value of migratability of ENP with a radius of 5 nm in LDPE at 25 °C for the contact between packaging and food over one year is 1.3×10^{-6} m. Further assume that the ENPs migrate from LDPE polymer sheet of a thickness of $h = 50 \mu\text{m}$ to the food of the volume of 1 dm^3 and that the value of distribution coefficient is $K = 1$. Comparing the volume of packaging to the volume of food, in the equilibrium practically all the nanosilver should migrate to the food. Provided that the initial concentration of silver ENPs in the packaging is $c_0 = 1 \text{ kg.m}^{-3}$ and the packaging surface is $S = 0.2 \text{ m}^2$, it can be evaluated from Eq. (12) that the equilibrium would be established after more than 1500 years. This is the estimation for the highest migratability encountered in Tab. 3. The time estimated for other polymers would be even longer. This example shows that the equilibrium distribution of ENPs between packaging and food will not be established within the useful lifetime of the products.

CONCLUSIONS

A contributing factor to the rapid commercial development in nanocomposite-based food packaging materials is the expectation that, due to the fixed or embedded nature of ENPs in plastic polymers, they will not pose any significant risk to the consumer. However, experimental data on

migration of ENPs to provide confidence in such a proposition have so far been lacking. This paper is an essay on how the migration of ENPs from polymer packaging to food could proceed, taking into account the physicochemical properties of both the ENPs and the packaging materials. From these properties, some general characteristics and extent of the migration can be predicted.

The results indicate that the migration of ENPs from packaging to food will be detected mainly in the case of very small ENPs with the radius in the order of magnitude of 1 nm from the polymer matrices that have a relatively low dynamic viscosity and that do not interact with the ENPs. These conditions could be met in the case of nanocomposites of silver with polyolefines (LDPE, HDPE, PP). For bigger ENPs that are bound in polymer matrices with relatively high dynamic viscosities, the migration will not be detectable. This corresponds to nanosilver composites with PET and PS, and surface-modified montmorillonite embedded in various polymer matrices.

These predictions are in full agreement with the results of recent pioneering and extensive experimental testing that has been carried out at Central Science Laboratory (United Kingdom) into migration of ENPs from two FCMs made of nanocomposites (Q. Chaudhry, unpublished). As predicted by this article, the results of the migration testing showed no detectable migration of clay minerals from beer bottles that had nanoclay-composite embedded between PET layers. The second FCM tested was the food containers made of polypropylene-nanosilver composite. Again, as predicted, there was only a very low level of migration of silver, which was less than the method's limit of quantification. In either case, the presence of ENPs did not show any significant changes in the migration of non-nanocomponents from the polymer. Whilst the results of migration testing provide a confirmation of the conclusions drawn in this article, more testing on other types of nanocomposites would be needed to build a broader picture and to confirm the predicted migration patterns for other nanocomposites. It is, however, worth noting that, on the basis of predicted migration of ENPs from nanocomposite-based FCMs and the limited migration data available, it appears that this application area of nanotechnology may indeed not carry any significant risk of ENP exposure for an average consumer.

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