

Nanocomposite Materials for Food Packaging Applications: Characterization and Safety Evaluation

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Abstract Food packaging requires long shelf life and the monitoring of safety and quality based on international standards. In the past decade, polymer nanocomposites have emerged as a new class of food packaging materials, because they have several advantages, such as enhanced mechanical, thermal, and barrier properties. The larger surface area of nanoparticles compared with their microscale counterparts favours filler–matrix interactions and the performance of the resulting material. A new technology is accepted by the community once it has been tested for its effects on health. There have been some studies on the migration of nanoparticles from packaging material into food/food simulants during storage. It is very important to evaluate the safety of nanocomposite packaging materials used for food products. This review summarizes the characteristics and properties of nanocomposite packaging materials along with their safety problems for food consumers.

Keywords Nanocomposite · Food packaging · Characterization · Safety · Migration

Introduction

Over the last few decades, the application of polymers as food packaging materials has increased enormously due to their advantages over other traditional materials [68].

Nowadays polymers reinforced by micrometre fillers are being used to obtain higher strength and stiffness, to improve solvency or fire resistance, or simply to reduce costs. The incorporation of these micro-sized fillers, however, has some drawbacks, such as brittleness and opacity. However, it is better to note here that opacity is not a trivial parameter in the packaging of light-sensitive food products such as vegetable oils and fruit juices. Nanocomposites, for which at least one dimension of the filler is in the nanometre range, overcome the limitations of traditional fillers [153]. Additionally, the improvements in nanocomposite properties achieved at very low loading level (<5 wt%) of fillers, while the microcomposites usually require much higher loadings (25–40 wt%) [157]. Using trace amounts of nanoparticles in packaging materials causes the final product to be less expensive, and that is satisfactory for the ultimate consumers. Polymeric materials are used extensively in food packaging, because they are lightweight and cheap. Among the various polymeric packaging materials, polyethylene terephthalate, polyethylene, and polystyrene are those most commonly used in food packaging systems. Significant research has been done using nanoparticles on the characteristics of these polymers (see Table 1). The PET nanocomposite process is more complex than that of polyethylene or polystyrene. PET is a moisture-absorber polymer, and its mixing with nanoparticles via an extruder is difficult. It is brittle and cannot be mixed with nanoparticles in large quantities. Polyethylene is structurally the simplest plastic and is made by adding polymerization of ethylene gas in a high temperature and pressure reactor. Polyethylenes can be made into strong, tough films with good barrier properties to moisture and water vapour. Compared with other plastics, polyethylenes do not provide a good barrier to oils/fats and gases like oxygen and carbon dioxide, although their barrier

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Table 1 Some examples of researches done on polymer nanocomposites

Polymer type	Nanoparticle(s)	Findings	References
Polyethylene terephthalate	Organoclay	Nanoparticles improved the thermal stability and the tensile mechanical properties of PET hybrid fibres	[28]
	Nanoclay	The morphology of nanocomposites altered depending on the nature of the filler and the surfactant. The morphology of nanocomposites showed a range from very good nanoscale dispersions (mostly delaminated nanocomposites) to rather poor dispersions (conventional microcomposite) depending on the nature of the filler and the surfactant	[38]
	Montmorillonite, TiO ₂ , and SiO ₂	Montmorillonite and TiO ₂ behaved as nucleating agents for PET, while SiO ₂ acted as inhibitor. According to mechanical test, the addition of nanoparticles had a slight influence on the elastic modulus and yield stress	[178]
	Montmorillonite, titanium oxide, silica	All nanocomposites showed better thermal and mechanical properties in comparison with the neat PET	[179]
	TiO ₂	The results of tensile test show that elongation at break and dissipated energy increase with additions of TiO ₂ nanoparticles into PET and PLA matrices that reach the maximum amount at 3 % loading level of TiO ₂	[51]
	Modified montmorillonite	PET/montmorillonite nanocomposites had better mechanical and gas barrier properties, while the nanofillers did not alter the degree of crystallinity	[95]
	Nanoclay, TiO ₂	Spherical and plate-like nanoparticles showed difference behaviour in polymer matrix. The results showed that plate-like nanoparticles broader surface area had more significant effect on crystallization rate than spherical nanoparticles	[54]
Polyethylene	Nanoclay	The flammability of the PE/clay nanocomposites was greatly improved due to the formation of the clay-enriched protective char during the combustion	[201]
	Nanoclay	The resultant nanocomposite, even in small clay loading level (0–10 wt%), showed higher modulus, strength, and the other physical properties	[149]
	Nanoclay	Polyurethane/clay nanocomposite films were evaluated as potential barrier membranes to gas permeation	[69]
	Montmorillonite	The rate of photo-oxidation increased with an increase in the clay concentration due to the presence of Fe in MMT	[85]
	Nanoclay	All the prepared nanocomposites exhibited a significant improvement in elastic modulus and toughness compared to pristine LDPE/LLDPE blends of the same composition. Thermal stability of nanocomposites in the air and nitrogen atmosphere was improved	[67]
	Nanosilver	PE/AgNps nanocomposites prepared by in situ polymerization were effective against E. Coli, with dependence on the amount of the silver nanoparticle added and on contact time	[196]
	Silica nanoparticles	A significant increase in the elastic modulus and elongation at break due to nanofiller introduction was observed	[45]
	TiO ₂	Mechanical properties of LDPE/modified TiO ₂ nanocomposites improved in comparison with the original, LDPE/unmodified samples	[127]
Polystyrene	Clay	Thermal and mechanical properties of nanocomposites were improved drastically with lower clay loading of up to 3wt%	[181]
	Oligomerically modified clay	The results show a mixed immiscible/intercalated/delaminated morphology. The maleic anhydride modified clay improved the compatibility between the clay and the polystyrene	[202]
	Calcium phosphate nanoparticles	The storage modulus increased with respect to the filler loading, and the glass transition temperature showed a positive shift indicating good reinforcement	[159]
	Silica	Mechanical properties indicate the presence of crystalline structure due to strong decrease of elasticity	[77]
	Silica	The best improvement of mechanical and thermophysical properties is achieved for nanocomposites containing 5 wt% silica nanoparticles	[154]
	Montmorillonite	The prepared nanocomposites have antimicrobial and antioxidant properties, and the researchers believe that they can play an important role for some biomedical applications	[65]

properties improve with density. Their heat resistance is lower than that of other plastics used in packaging, with a melting point of around 120 °C, which increases with density [34].

Polystyrene has many packaging applications and can be extruded as a monolayer plastic film, coextruded as a thermoformable plastic sheet, and injection moulded and foamed to give a range of pack types. It is also copolymerized to extend its properties. It is less well known as an oriented plastic film, though the film has interesting properties. It has high transparency (clarity), and it is stiff, with a characteristic crinkle, suggesting freshness, and has a deadfold property [34]. When these polymers are combined with nanoparticles, the resulting nanocomposite may have better properties than the neat polymer. Some examples are shown in Table 1. Generally, results of these studies indicate that polymer nanocomposites have better mechanical, thermal, and barrier properties than the neat polymer. From the standpoint of processing, polyolefins, like polyethylene and polystyrene, need a lower temperature and shearing force than PET when they are mixing with compatible nanoparticles in an extruder. Besides the advantages of nanocomposite packaging, their safety also deserves attention. To satisfy the increasing expectations of consumers, food must be safe, must have consistently good quality and sensory attributes, and should have a good shelf life [80, 146]. The application of nanocomposites for food packaging and their characteristics have been well studied [9, 12, 24, 71, 151, 167], but there is not enough evidence to ensure the safety of nanocomposite packaging materials in the case of food application. This study presents an overview of nanoparticle types used in food packaging systems, describes the properties of polymer nanocomposites, and explains recent developments in nanopackaging systems and the safety of nanocomposites in food packaging systems.

Nanoscale Reinforcements for Food Packaging

Nanoreinforcements are nanoscale fillers that are dispersed into a specific matrix during processing. The ratio of the largest to the smallest dimension of filler is an important property known as aspect ratio (Fig. 1).

Clays and Silicates

The packaging industry focuses substantially on layered inorganic nanoparticles like clays and silicates. They are generally available and need simple processing [12]. In contrast to the typical tactoid structure of microcomposites in which the polymer and the clay tactoids remain immiscible [5, 103], the interaction between layered silicates and polymers may produce two types of nanoscale

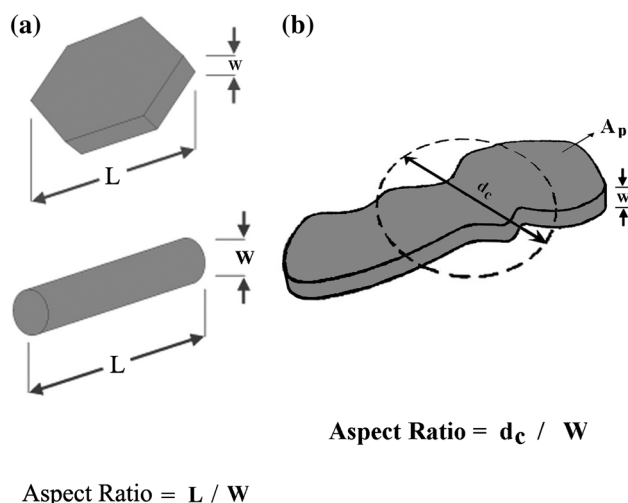


Fig. 1 Aspect ratio of regular (a) and irregular (b) nanoparticles

composites, namely intercalated nanocomposites, which result from the penetration of polymer chains into the interlayer region of clay, and exfoliated nanocomposites, which involve extensive polymer penetration. Intercalated nanocomposites produce an ordered multilayer structure with alternating polymer/inorganic layers, while in exfoliated nanocomposites clay layers delaminate and randomly disperse in the polymer matrix [103, 186]. Due to optimal clay–polymer interactions of exfoliated nanocomposites, they exhibit somewhat better properties [1]. Montmorillonite (MMT) is a clay most commonly used in the preparation of polymer nanocomposites. It is a member of the smectite group and is a 2:1 clay, meaning that it has 2 tetrahedral sheets sandwiching a central octahedral sheet [186]. The imbalance of the negative surface charge is compensated by exchangeable cations (typically Na^+ and Ca^{2+}). The parallel layers are linked together by weak electrostatic forces [171]. This type of clay is characterized by a moderate negative surface charge (cation-exchange capacity, CEC), which is an important factor in defining equilibrium layer spacing. The charge of the layer is not locally constant as it varies from layer to layer. Rather, it must be considered as an average value over the whole crystal [6]. Montmorillonite provides suitable properties for polymers due to its high surface area and fairly large aspect ratio (50–1000) [182].

Titanium Dioxide (TiO_2)

Among many different types of nanoscale fillers, TiO_2 nanopowder is increasingly being investigated because it is chemically inert, has broadband UV filter properties, is antibacterial from its photo-irradiation effect, is corrosion resistant, has a high level of hardness, has a high refractive

index, and is inexpensive [166]. In nature, titanium dioxide exists in three primary phases—anatase, rutile, and brookite—with different sizes of crystal cells in each case [121].

TiO₂ maintains its photocatalytic abilities. Nanoscale TiO₂ has a surface reactivity that fosters its interactions with biological molecules, such as phosphorylated proteins and peptides [97], as well as some non-specific binding with DNA [25]. Nano-anatase TiO₂, which is smaller than 20 nm, has surface corner defects that alter the size of the crystal cell [143] (Table 2). The surface energy of TiO₂ nanoparticles is an important parameter in polymer/filler interaction. Naicker et al. [121] reported that the surface energy of a TiO₂ nanoparticle increases and approaches a constant value as the particle gets bigger. The surface energies of small rutile particles are higher than those of anatase particles of a similar size, consistent with anatase being the more stable phase of nanocrystalline titanium dioxide [121]. In recent years, TiO₂ has been widely used in preparing different types of nanomaterials, including nanoparticles, nanorods, nanowires, nanotubes, and mesoporous and nanoporous TiO₂-containing materials [30]. The effects of nanoscale TiO₂ on crystallization and the viscoelastic behaviour of synthetic and natural polymers have been discussed in some researches [51, 96, 102, 123, 178, 179, 193]. Depending on the polymeric matrix type, the addition of TiO₂ nanoparticles could either increase [193] or decrease [102, 123] the degree of crystallinity of nanocomposites. Other parameters like melting point, glass transition, and crystallization rate could also change according to polymer structure [150]. The antibacterial mechanism of TiO₂ was studied by several researchers [8, 29, 106, 116]. The antibacterial ability of nano-TiO₂ is mainly dependent upon UV irradiation, which limits its application [161].

Silica (SiO₂)

Silica nanoparticles (nSiO₂) have been reported to improve the mechanical and/or barrier properties of several polymer matrices. Wu et al. [190] observed that the addition of nSiO₂ into a polypropylene (PP) matrix improved the tensile properties of the material—not only strength and modulus, but also elongation [190]. Xiong et al. [191] were also found that addition of nSiO₂ into starch matrix could

improve the tensile properties of nanocomposites [191]. They also observed that an nSiO₂ addition decreased water absorption by starch. Vladimirov et al. [184] incorporated nSiO₂ in an isotactic polypropylene (iPP) matrix, using maleic anhydride grafted polypropylene (PP-g-MA) as a compatibilizer [184]. nSiO₂ increased the storage modulus of iPP, making the material stiffer, and improved the oxygen barrier of the matrix. Jia et al. [74] prepared nanocomposites of PVOH with nSiO₂ by radical copolymerization of vinyl silica nanoparticles and vinyl acetate [74]. The nanocomposites had improved thermal and mechanical properties when compared to pure PVOH, due to strong interactions between nSiO₂ and polymer matrix via covalent bonding. Tang et al. [172] prepared starch/PVOH/nSiO₂ biodegradable films [172]. With the increase in nSiO₂ content, the tensile properties and water resistance of the films were improved. There was also an increase in the intermolecular hydrogen bonds as well as the formation of C–O–Si groups, between nSiO₂ and starch, or nSiO₂ and PVOH, which improved the miscibility and compatibility between film components. Some authors [190, 200] observed that the presence of grafting polymers on the surface of nSiO₂ improved the tailorability of the composites; that is to say, different species of grafting monomers result in different interfacial interactions and tensile properties [190, 200]. Investigations have shown that SiO₂ nanoparticles can form a twisting path for gases when they are used as fillers in food packaging materials. They can also improve the mechanical properties, especially tensile properties, of nanocomposite films.

Silver Nanoparticles

The unique antimicrobial properties of silver nanoparticles have made them one of the most commercialized nanomaterials in health care [20, 31]. Its antibacterial properties make it attractive in food packaging [99]. This antibacterial activity, however, is undesirable when nanosilver is disposed of and ends up dissolving and leaching ions [49, 86, 91], which act against aquatic microorganisms [48]. Regulatory agencies worldwide monitor nanosilver [125], which has prompted research for a detailed understanding of its toxicity [48, 125]. In this way, correct risk assessments can be made and its safe use can be established for minimal, if any, environmental impact. There is an ongoing debate regarding the role of released Ag⁺ ions from nanosilver and its toxicity to microorganisms [180]. More specifically, Navarro et al. [124] concluded that nanosilver alone has minimal toxicity, and it serves mostly as a source of Ag⁺ ions. Miao et al. [110] also showed that dissolved Ag⁺ ions dictate nanosilver's toxicity. In contrast, Fabrega et al. [49] concluded that the effect of released Ag⁺ ions is not significant, and thus, the dominating factor for this

Table 2 Phases of TiO₂ [121]

Phases	Crystal systems	a (Å°)	b (Å°)	c (Å°)
Rutile	Tetragonal	4.594	4.594	2.959
Anatase	Tetragonal	3.789	3.789	9.514
Brookite	Orthorhombic	9.166	5.436	5.135

toxicity is bacterial contact with the nanosilver particles themselves. Furthermore, Kawata et al. [78], in agreement with Laban et al. [86], also stated that the toxicity induced by nanosilver cannot be attributed solely to the released Ag^+ ions, but rather to nanosilver particles. All these studies, however, employed commercially available nanosilver [78, 110, 124] and had limited, if any, control over Ag size, morphology, and degree of agglomeration. This makes drawing universally accepted conclusions regarding the mechanism of nanosilver toxicity difficult. For example, it is not uncommon to have nanosilver flocculation in bacterial suspensions unless its surface is modified with surfactants [26] that may alter again the antibacterial activity of nanosilver. The results showed that not only must the antimicrobial properties of Ag nanoparticles be taken into account, but also the detrimental effect of ionized silver on biological cells should be considered. This effect is observed when direct contact between particles and cells occurs. In the last few years, food contact materials containing nanosilver have been widely used. The ubiquitous use of such commercial products may potentially compromise the health of many organisms, because food contact materials containing nanosilver may release silver nanoparticles into foods [72].

Cellulose-Based Nanoreinforcements

Cellulose nanoreinforcements (CNRs) are intensively discussed because of their low cost, lightweight, and high strength [66, 141]. Cellulose chains are synthesized in living organisms (mainly plants) as microfibrils (or nanofibres), which are bundles of elongated molecules (with 2–20 nm in diameter and micrometric in length) stabilized by hydrogen bonds [14, 109, 133]. Each microfibril, formed by elementary fibrils, has crystalline and amorphous regions. The crystalline parts, which may be isolated by procedures such as acid hydrolysis, are the nanocrystals or nanowhiskers [15, 46], whose aspect ratios are related to the origin of the cellulose and processing conditions. Thus, a microfibril can be considered as a string of whiskers linked by amorphous domains, which are taken as structural defects. Azeredo et al. [13] studied the influence of cellulose nanofibres on the physical properties of chitosan films. In their study, mechanical and water vapour barrier properties of chitosan films were improved by adding cellulose nanofibres. The authors proved that a nanocomposite chitosan film with 15 % cellulose nanofibres and plasticized with 18 % glycerol was comparable to synthetic polymers in terms of strength and stiffness, but its elongation and water vapour barrier were poorer. They believe that the film may be used only for applications that

do not require great flexibility and/or a water vapour barrier [13]. Khan et al. [79] investigated the mechanical and barrier properties of nanocrystalline cellulose/chitosan films. The mechanical properties of the nanocomposite were improved by the formation of a percolating network and strong filler–matrix interaction. A 27 % reduction in WVP was obtained because of the incorporation of only 5 % NCC. The authors believe that NCC-reinforced nanocomposite films, because of their excellent mechanical and barrier properties, should have a promising impact on food packaging in the coming years [79]. In general, it can be said that cellulose nanoparticles are of great importance in improving the mechanical properties of natural polymers. From the standpoint of safety, it seems that the cellulose nanoparticles have less risk on consumer safety, because of their natural origin.

Characterization of Nanocomposites

There is a need for characterization techniques to better understand the structure of nanocomposites. Characterization methods enlighten us about nanoparticle dispersion in the polymer matrix, interactions between nanofillers surface and polymer chains, and the effects of process parameters on the final properties of nanocomposites. In many cases, it is necessary to apply more than one characterization technique to obtain accurate data on nanocomposite material. For instance, the X-ray diffraction (XRD) technique was initially used to identify the intercalated/exfoliated structures of the polymer/clay nanocomposites, while it was shown that X-ray diffraction alone is not enough to identify the morphology of a nanocomposite. In fact, the use of XRD alone can be misleading since both exfoliated and disordered structures will show no peak [199]. Additional techniques are needed to get accurate and comprehensive information about nanocomposite morphology. Generally, to have a better view of the microstructure of nanocomposites, synergistic combinations of different characterization techniques are useful. A number of nanocomposite characterization methods are available, which include differential scanning calorimetry, thermogravimetric analysis, transmission electron microscopy, scanning electron microscopy, X-ray diffraction [117, 118, 145], nuclear magnetic resonance [92, 155], IR spectroscopy, Raman spectroscopy [44], X-ray photoelectron spectroscopy [107], dielectric relaxation spectroscopy [111], atomic force microscopy [2, 122]. In addition, some of the techniques are used to evaluate the properties of nanocomposites, like mechanical performance [136, 177], barrier performance [21, 168], thermal properties [37, 115]. The following is a description of some of the mentioned properties.

Barrier Properties of Nanocomposites

The improved barrier properties of polymer–clay nanocomposites result from the increased tortuosity of the diffusive path for permeants (Fig. 2). It forces them to travel a longer path to diffuse through the film. In relation to food packaging, the presence of high aspect ratio nanoparticles in the packaging decreases the transfer rate of the gasses like oxygen, carbon dioxide, and water vapour crossing the package. This theory was developed by Nielsen [128] and was further corroborated by other authors [1, 114]. The increase in path length is a function of the aspect ratio of the clay and the volume fraction of the filler in the composite (see Eq. 1). Nielsen's model has been used effectively to predict the permeability of systems at clay loadings of less than 1 %, but some experimental data have reported much lower permeability than predicted at higher loadings [1]. Beall [17] proposed a new model to predict the permeability of nanocomposites focusing on the polymer–clay interface as an additional governing factor to the tortuous path, thus providing a correction factor to Nielsen's model [17]. Conventional composites had a less restrictive path for gas penetration in their microstructure [194]. Sanchez-Garcia et al. [156] showed that novel PET nanocomposites had enhanced barrier properties to oxygen and water [156]. The barrier properties of corn zein nanocomposite coated polypropylene films for food packaging applications were improved by incorporating layered silicates [135]. The water vapour permeability of starch–clay nanocomposites was also improved rather than neat starch film [135, 137, 156, 173].

High aspect ratios of nanoparticles could provide large surface areas with better reinforcing effects [14, 41]. On the other hand, a change in the size and number of particles per unit volume of polymer will have a significant impact on the properties of bulk polymer [75]. Equation (1) shows

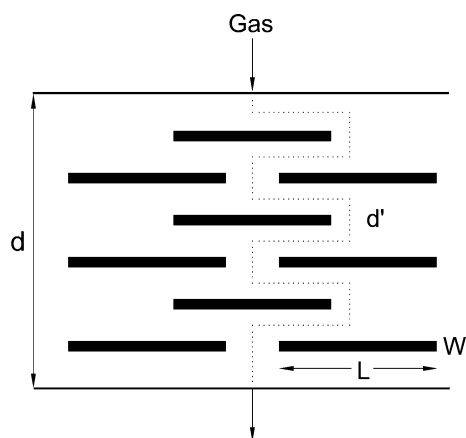


Fig. 2 Definition of tortuosity factor

the relation between the aspect ratio, volume per cent, and barrier property of nanocomposite packages [33]:

$$\frac{P}{P'} = \frac{1}{1 + \frac{1}{2\phi} \cdot \left(\frac{L}{W}\right)} \quad (1)$$

where L/W is the aspect ratio of nanocomposites, ϕ is the volume percentage of nanoparticles in the polymer matrix, P is the permeability of neat polymer, and P' is the permeability of polymer nanocomposite. For irregular objects, we define the aspect ratio as d_p/w , where d_p is projected area diameter (see Fig. 1b). So d_p results from the microscopically measured area A_p using Eq. (2). [18, 57]:

$$d_p = \left(\frac{4A_p}{\pi}\right)^{1/2} \quad (2)$$

The tortuosity factor (τ) is defined as the distance travelled by a permeant molecule (d') to the thickness of the sample (d) (see Fig. 2).

$$\tau = \frac{d'}{d} = 1 + \frac{1}{2\phi} \cdot \left(\frac{L}{W}\right) \quad (3)$$

A higher aspect ratio of nanoparticles increases the value of d' and finally enhances the tortuosity factor.

Crystallinity and Thermal Properties of Nanocomposites

Nanoparticles can improve the thermal properties of food packaging polymers if they are well dispersed in the polymer matrix. Glass transition point (T_g) and crystallinity are two important parameters in evaluating the thermal properties of polymers. Nanoparticles may elevate or diminish the T_g of polymer. When the polymer chains are intercalated into plate-like nanoparticles (like clays and micas), they are confined in movement and T_g increases, while the exfoliation structure may not alter the T_g of a polymer nanocomposite. On the other hand, agglomerated nanoparticles decrease the polymeric network strength, and that can lead to a decrease in T_g . Once the nanoparticles are agglomerated, the interaction is more between the particles than the particle and the polymer [152].

The crystallinity (X_c) of plastic packaging materials is reported to increase with incorporation of nanoparticles into polymer matrix. Increases in X_c and the crystallization rate of nanocomposites could be caused by the heterogeneous nucleation effect of the nanoparticles' surface on the crystallization of polymer macromolecules, which reduces the need for meeting the barrier activation energy of thermal homogeneous nucleation. Therefore, the crystallization process of nanocomposites can begin at a higher temperature than that of pure polymer. Compared to spherical nanoparticles, the broader nucleation effect of platelet-like nanofillers with a superior aspect ratio resulted in higher crystallization of the polymer matrix [54, 93].

Mechanical Properties of Nanocomposites

Nanoparticles have the potential to improve the mechanical properties of a polymer even at low loading levels. Incorporation of nanoparticles in the polymer matrix significantly affects the mechanical properties of both synthetic and natural polymers [51, 66, 67, 79]. The elastic modulus of nanocomposites increases with the addition of mineral rigid nanoparticle, while the ductility of polymer may alter based on nanoparticle type. Farhoodi et al. [54] showed that PET nanocomposite's ductility was enhanced by the addition of spherical TiO₂, yet reduced with the addition of nanoclays [54]. The reinforcing effect of TiO₂ nanoparticles on polymer ductility could be a consequence of the creation of new energy damping mechanisms in the presence of nanoparticles, such as agglomerates breaking up, void nucleation, crack deflection, nanofiller debonding or pull out, matrix deformation and bridging [170].

New Aspects of Application of Nanocomposites in Food Packaging

In addition to improving thermal, mechanical, and barrier properties, etc., new applications of nanocomposites in the food industry (like nanosensors and nanoscale enzyme immobilization systems) can also be noted.

Nanosensors

Nanosensors can be incorporated into food packaging matrices which have the ability to identify specific microbial and/or chemical contaminants or environmental conditions [39]. The main objective of nanosensors is to reduce the time of detecting pathogens in foodstuffs [22]. Nanosensors are introduced as an electronic tongue or nose embedded into packaging material, and they detect chemicals released during food spoilage [58, 61, 100]. "Microfluid" nanosensors are devices that can also be used to efficiently detect pathogens in real time and with high sensitivity. Major advantages of microfluidic sensors are their miniature format and their ability to rapidly detect compounds of interest in only microlitres of required sample volumes, which has already led to widespread applications in medical, biological, and chemical analysis [16, 105].

Detection of Gases (Gas Indicators)

Excessive amounts of some gases such as oxygen and water vapour cause food spoilage. The diagnosis of gases in packaging requires the destruction of the package structure [165, 192]. Moreover, performing such tests is time-consuming and costly. Therefore, a non-invasive leak

detection method would be valuable for monitoring the gas content of a package.

Luechinger et al. [104] developed a highly sensitive optical method for detecting humidity [104]. They suggest such humidity sensors in large-scale applications for food handling, storage, and transport. In this method, porous metal films for optical humidity sensing were prepared from copper nanoparticles protected by a 2- to 3-nm carbon coating, a silicon tenside, and a polymeric wetting agent. Exposure to water or solvent vapour revealed an exceptional sensitivity with optical shifts in the visible light range of up to 50 nm for a change of 1 % in relative humidity. Mills [112] developed a promising photo-activated indicator ink for detecting oxygen in packaging based upon nanoscale TiO₂ or SnO₂ particles and a methylene blue redox-active dye [112]. The colour of the detector gradually changes in response to small quantities of oxygen. Vu and Won [185] developed a water-resistant UV-activated oxygen indicator using thionine, glycerol, P25 TiO₂, and zein as a redox dye, a sacrificial electron donor, a UV-absorbing semiconducting photocatalyst, and an encapsulation polymer [185]. This novel water-resistant UV-activated oxygen indicator was also successfully photo-bleached and regained colour rapidly in the presence of oxygen.

Nanoscale Enzyme Immobilization Systems

Due to high-surface-area-to-volume ratio of nanoparticles, they can lead to reactions at a much faster rate than larger particles of equal mass. Nanoscale immobilization systems would have strongly intensified performance, since they would increase the available surface contact area and modify the mass transfer, probably the most important factors affecting the effectiveness of such systems [56]. Enzymes immobilized to nanoscale scaffolds, such as spheres, fibres, and tubes, have recently been reported [81, 108, 195]. Qhobosheane et al. [142] immobilized lactate dehydrogenase (LDH) and glutamate dehydrogenase onto silica nanoparticles in order to modify them biochemically. The immobilized preparations showed excellent enzymatic activities and detection capabilities [142]. Gopinath and Sugunan used acid-activated montmorillonite (K 10) as support. The enzymes α -amylase, glucoamylase, and invertase were immobilized onto montmorillonite via two independent techniques (adsorption and grafting) using glutaraldehyde as spacer [62]. According to the above findings, nanomaterials could create new opportunities for stabilizing enzymes with improved intrinsic and operational stabilities. These materials could develop available surface contact area, multiple sites for interaction, and reduced mass-transfer limitations.

Time Temperature Logs

Time temperature logs have the potential to assist in product biosecurity and traceability [50, 134, 162, 164, 174, 175, 188]. Deviations from food storage conditions could lead to premature deterioration of the food and may even endanger consumer safety due to the presence of toxins or pathogens. The rate of change of visual indication in a time–temperature indicator must be temperature dependent and increase at higher temperatures similar to most physicochemical reactions. The major mechanisms upon which the TTIs are based include enzymatic reaction, polymerization, melting point, and diffusion of a substance [140]. Due to their large surface area, nanomaterials prepare rapid visual responses when they are applied as indicators in packaging systems. They also provide a reliable indication of product quality and residual shelf life regardless of the temperature history [198]. The nanocrystal-based indicators provide a number of merits, including lower cost, ease in production, and simpler for detection by either the naked eye or a UV/Vis spectrometer [197].

Preparation of Nanocomposites

Nanocomposites are generally prepared by the following methods:

1. **Exfoliation–adsorption:** The layered silicate is exfoliated into single layers using a solvent, in which the polymer (or a prepolymer in the case of insoluble polymers such as polyimide) is soluble. It is well known that such layered silicates, owing to the weak forces that stack the layers together, can be easily dispersed in an adequate solvent. The polymer then adsorbs onto delaminated sheets and, when the solvent is evaporated (or the mixture precipitated), the sheets reassemble, sandwiching the polymer to form, in the best case, an ordered multilayer structure. This process also includes the emulsion polymerization where the layered silicate is dispersed in the solution [6].
2. **In situ intercalative polymerization:** The in situ method, also known as interlamellar polymerization, involves swelling of the layered silicates by absorption of a liquid monomer or a monomer solution. The monomer migrates into the galleries of the layered silicate, so that polymerization can occur within the intercalated sheets. Polymerization can be initiated either by heat or radiation, by diffusion of a suitable initiator, or by an organic initiator [6, 90].
3. **Melt processing:** In this technique, no solvent is required [43, 148] and the layered silicate is mixed within the polymer matrix in the molten state. A thermoplastic polymer is mechanically mixed by

conventional methods such as extrusion and injection moulding with organophilic clay at an elevated temperature [83]. The polymer chains are then intercalated or exfoliated to form nanocomposites. This is a popular method for preparing thermoplastic nanocomposites. The polymers, which are not suitable for adsorption or in situ polymerization, can be processed using this technique.

Safety Evaluation of Nanocomposite Food Packaging

To ensure protection of the health of the consumer and to avoid adulteration of the foodstuff, migration tests were performed on packaging materials. Two types of migration limits have been established in the area of plastic materials: an overall migration limit (OML) of 60 mg (of substances)/kg (of foodstuff or food simulants), which applies to all substances that can migrate from food contact material to foodstuff, and a specific migration limit (SML), which applies to individual authorized substances and is fixed based on the toxicological evaluation of the substance. The SML is generally established according to the acceptable daily intake (ADI) or the tolerable daily intake (TDI) set by the European Food Safety Authority (EFSA). To set the limit, it is assumed that, every day throughout his/her lifetime, a person of 60 kg eats 1 kg of food packed in plastics containing the relevant substance at the maximum permitted quantity (according to European Union standards). New technology, however, requires testing in order to identify any problems that may be associated with the product. There have been many studies done on the migration of monomers, plasticizers, and other additives from PET [10, 27, 52, 76, 138, 187, 189], polystyrene [42, 59, 94, 98, 113, 120, 129, 130, 139, 144], and polyvinyl chloride [3, 4, 7, 19, 55, 63, 203] into food/food simulants. These polymers are commonly used as packaging material for food products. Polyolefins (like polystyrene, polyvinyl chloride.) are more hydrophobic and typically exhibit surface tensions around 30 dynes/cm versus polyester that is around 40–44 dynes/cm. The hydrophobic nature of polyolefin allows for a broad selection of additives, many of which are incompatible and readily migrate to the surface. Polyesters (like PET), however, are more polar and typically have a better level of compatibility with the additives, so less migration occurs. Nanofillers in food packaging are generally inorganic materials, which are incompatible with the polymer matrix. They are not thermodynamically stable, so they tend to diffuse across the polymeric packaging film. Recently, there have been studies on the migration of nanoparticles from nanocomposite packaging materials into food/food simulants (see Table 2). Avella et al. [11] observed the low-level

migration of nanoclay constituents such as silicon from biodegradable starch/clay nanocomposite films into distilled water [11]. The details of their experiment are shown in Table 2. The authors concluded that, after contact of the nanocomposite films with both vegetables (lettuce and spinach), higher Si contents were observed that could easily be attributable to the fact that clay nanoparticles are mainly composed of this element. A theoretical research was carried out from a physicochemical point of view, of which the results indicated that the migration of nanoparticles from packaging to food is detected only in the case of very small particles within a radius of 1 nm from the polymer matrices, and for bigger nanoparticles, the migration is not detectable [163]. This study did not actually consider the effect of the food/food simulant on the structure of the packaging material, which is a substantial parameter in the migration phenomenon. Huang et al. [72] investigated the migration of Ag from polyethylene plastic bags into food simulants using a method of atomic absorption spectroscopy (AAS) [72]. SEM/EDX and AAS analyses by the authors of this study highlighted evidence of nanosilver migration from polyethylene bags into food-simulating solutions. They found that nanosilver could migrate from one kind of commercial available food contact plastic bag into food-simulating solutions representing water, acid, alcohol, and fatty foods. The authors believe that the migration size of nanosilver (≤ 300 nm) is a hazardous dimension to the safety of organisms. Therefore, the potential risks of nanosilver are currently preventing scientists and the public from fully supporting the advancement of nanosilver technology [72]. Farhoodi et al. [53] investigated the migration of aluminium and silicon from PET nanocomposites bottles containing 3 wt% nanoclays into an acidic food simulant [53]. TEM micrographs of PET sheets containing 3 wt% nanoclays showed a partially exfoliated/intercalated structure with dispersed tactoids. It is important to survey the morphology in the case of platelet-like nanocomposites like clays and micas. When polymer chains intercalate into the interlayer of nanoclay, there will be a strong interaction between the polymer chains and the surface of nanoclay particles, which could result in less migration of nanoparticles into the contact solution. Then, exfoliation structures could result in a higher level of nanoclay migration. The results of the ICP test showed that there was more migration of Al and Si with longer storage times and at higher temperatures. Concentrations of aluminium in the food simulant after 90-day storage at 25 and 45 °C were 0.18 and 0.34 ppm, respectively. Silicon concentrations in the food simulant after the same storage times and temperatures increased to 6.0 and 9.5 ppm, respectively [53]. Cushen et al. [40] investigated the migration of silver and copper nanoparticles from polyethylene nanocomposites to boneless chicken

breasts [40]. Silver and copper nanoparticles have been incorporated into polymers to create antimicrobial packaging materials. In this study, a migration model was developed on the basis of mathematical relationships defining migratability using the Williams–Landel–Ferry equation for time–temperature superposition [163]. The results showed that the quantities of silver in samples that had been in contact with the nanosilver PE composite (with a mean of 0.0041 mg/dm²; $n = 16$) were significantly different from the control samples (with a mean of 0.001 mg/dm²; $n = 8$) ($p < 0.001$). The samples in contact with the nanocopper PE composite had significantly higher copper levels (with a mean of 0.037 mg/dm²; $n = 16$) than the control samples (with a mean of 0.0157 mg/dm²; $n = 8$) ($p < 0.05$) but to a different level of significance than the silver experiments. The authors explained it by the presence of copper in chicken meat as a naturally occurring biological mineral [40].

Health Safety Aspects of Nanoparticles for the Consumer

With the rapid development of nanotechnology, detailed knowledge of interactions between nanoparticles and cells, tissues, and organisms has become progressively serious, particularly in relation to possible hazards to human health. Nanoparticles may march into the body via inhalation, ingestion, or cutaneous exposure. Once they have entered a biological milieu, nanoparticles will inevitably come into contact with a huge variety of biomolecules including proteins, sugars, and lipids that are dissolved in body fluids, such as the interstitial fluid between cells, lymph, or blood. It has been observed that smaller nanoparticles seem to be more toxic than larger ones [32]. Small nanoparticles possess a high surface area relative to their total mass, which increases the opportunity to interact with biological molecules around and, as a consequence, to trigger adverse responses [32, 160, 176, 183]. However, size is not the only factor that causes toxicity; other factors like surface functionalization also play important roles.

Cationic nanoparticles are considered more toxic than neutral or anionic ones, possibly due to their high affinity towards the negatively charged plasma membrane. Therefore, the toxicity of nanoparticles must be evaluated by systematically changing nanoparticles properties, one at a time [101]. Nel et al. [125, 126] investigated the lysosomal damage and the induction of cytotoxicity by cationic nanoparticles. Cationic particles bind with high affinity to lipid groups on the surface membrane and are endocytosed in the tight-fitting vesicles. Once these cationic nanoparticles enter into an acidifying lysosomal compartment, the unsaturated amino groups are capable of sequestering protons that are supplied by the ATPase (proton pump).

This process keeps the pump functioning and leads to the retention of one Cl^- ion and one water molecule per proton. Subsequent lysosomal swelling and rupture lead to particle deposition in the cytoplasm and the spillage of the lysosomal content [126] (Table 3).

Regulation of Nanotechnologies in the Food Packaging

It is obvious that the application of nanotechnology in food packaging is rapidly increasing, so it seems necessary to lay down regulations to ensure the safety of packaged products. The Institute of Food Science & Technology (IFST) has reiterated the deficiencies in current regulations concerning the impact of nanotechnology on food and packaging [73]. Food consumers need to have adequate information about food and its packaging (that includes type and size of nanoparticle, physicochemical properties of nanoparticle/nanocomposite, nanocomposite processing method, and safety concerns of nanomaterial/nanocomposite). The absence of a clear definition, public debate, food safety assessments, and proper food regulations may eventually jeopardize the potential benefits of nanotechnologies to food industry. Table 4 displays some toxicities resulting from nanoscale particles. Oral uptake from food with added nanoparticles and any migrations from the nanocomposites are the most significant exposure sources for human beings. The digested nanoparticles temporarily remain and accumulate in the gastrointestinal (GI) tract, and are then absorbed by the intestinal epithelium to be transported to other systems and organisms [64, 70]. The

Scientific Committee under EFSA has identified two specific hurdles in performing risk assessments on nanomaterials: difficulty in characterizing, detecting, and measuring nanomaterials and insufficient information on toxicology data [36]. The classification, labelling, and packaging of substances and mixtures are regulated by the Regulation (EC) No1272/2008. Users of hazardous substances and mixtures must be informed of the dangers by means of a new labelling system, which will include new safety symbols. Safety data sheets must also be made available to users. If a substance starts being produced at the nanoscale, a change could be brought about in the properties of the substance and therefore a change in its classification. As of December 2010, this type of information must be reported to the European Chemical Agency (ECHA). Although nanomaterials are not specifically mentioned, this regulation is a newly introduced hurdle with which chemical producers must contend in order to produce new substances. The Codex Alimentarius Commission, an intergovernmental agency established jointly by FAO and WHO, is promoting the coordination of all food standards work undertaken by international governmental and non-governmental organizations. In order to prevent regulatory gaps, the Codex Alimentarius Commission, participating in the development of international food safety regulations, should take into account the use of nanoparticles and other nanoscale technologies in food and agriculture. There are only a few international regulations of nanotechnology or nanoproducts. Only a few government agencies or organizations from different countries

Table 3 Experimental studies on the migration of nanoparticles into food/food simulant

Authors/ reference	Packaging material	Food/food simulant	Migration temperature	Total migration time	Nanoparticles	Detection method
Avella et al. [11]	Biodegradable starch	Lettuce and spinach (simulant: distilled water)	40 °C	10 days	Nanoclay constituents (silicon, iron, and magnesium)	Atomic absorption equipment
Huang et al. [72]	Polyethylene plastic bags	Simulant A (ultrapure water), Simulant B [4 % acetic acid (v/v)], Simulant C [95 % ethanol (v/v)] Simulant D (hexane)	Room temperature 40 °C 50 °C	15 days	Ag	SEM/EDX
Farhoodi et al. [53]	PET bottles	The acidic food simulant (acetic acid 3 % w/v)	25 °C 40 °C	90 days	Nanoclay constituents (silicon and aluminium)	Inductively coupled plasma- optical emission spectrometry (ICP-OES)
Cushen et al. [40]	Polyethylene	Boneless chicken breast	8.13 °C 21.8 °C	1.1 days 3.1 days	Silver nanoparticles (nanosilver) and copper nanoparticles (nanocopper)	

Table 4 Types of nanoparticles and cells interactions

Type of exposure	Type of nanoparticles	Findings	References
Inhalation	TiO ₂	Great pulmonary retention of TiO ₂ nanoparticles in rats was observed A great number of nanoparticles were found in the lymphatic ganglions, a phenomenon indicating penetration of the interstitial spaces	[131]
	Iridium nanoparticles	Radioactive iridium in the animals' liver, heart, and brain was observed Iridium nanoparticles were translocated to the organs, resulting in circulation of nanoparticles by the pulmonary blood vessels	[84]
	Carbon-13 nanoparticles	A large accumulation of carbon-13 in the livers of rats after exposure was observed. The researchers explained the liver concentration by translocation of nanoparticles from the respiratory system to the circulatory system and then to the liver	[132]
	Silver nanoparticles	The results of in vivo genotoxicity test after exposing to silver nanoparticles showed that exposure to silver nanoparticles by inhalation for 90 days does not induce genetic toxicity in male and female rat bone marrow in vivo	[82]
	Cerium oxide nanoparticles	These results suggest that acute exposure of CeO ₂ nanoparticles through inhalation route may induce cytotoxicity via oxidative stress and may lead to a chronic inflammatory response in rats	[169]
Cutaneous exposure	Titanium dioxide	The researchers did not observe significant absorption of coated TiO ₂ nanocrystals (17 nm), beyond the stratum corneum of the skin of human volunteers, except for a small quantity (<1 %), which had penetrated the hair follicles Since the follicles are also isolated from living tissue by a stratum corneum, the authors conclude that cutaneous absorption of TiO ₂ is absent in living cutaneous tissues	[87]
	Nanocrystalline TiO ₂	The researchers did not observe cutaneous absorption of nanocrystalline TiO ₂ in the skin layers below the corneum stratum in humans. These results suggest a low probability of absorption of nanoparticulate TiO ₂ beyond the dermis and its transport to the bloodstream	[158]
	Silver nanoparticles	The results showed that silver nanoparticles absorption through intact and damaged skin was very low, but detectable, and that in case of damaged, skin it was possible an increased permeation of silver applied as nanoparticles. Moreover, silver nanoparticles could be detected in the stratum corneum and the outermost surface of the epidermis by electron microscopy	[89]
	Silver nanoparticles	The results showed that permeation through glycerolized skin is significantly higher compared to both fresh and cryopreserved skin. This result can generate relevant clinical implications for burns treatment with products containing silver nanoparticles	[23]
Ingestion	Gold nanoparticles	The authors reported blood and tissue distribution of ingested colloidal gold nanoparticles in mice	[70]
	Au nanoparticle	The results obtained by Samuel on imaging angiogenesis by inter-intargeted paramagnetic iron oxide, demonstrated that cationic nanoparticles like Au can cause haemolysis and blood clotting, while usually anionic nanoparticles are quite non-toxic	[88]
	Silver nanoparticles	The results showed liver damage by a dysregulation of lipid metabolism, highlighting liver and heart as the most sensitive organs to the deleterious effects	[47]

have established standards and regulations to define and regulate the use of nanotechnology. The existing regulations of nanotechnology in some cases are discussed in Table 5. It should be noted that studies into the safety of nanotechnology and the development of nanoregulation among most countries are still mainly focusing on non-food nanomaterials and aspects. As the application of nanotechnology in the food industry is growing rapidly, it is foreseeable that research into its safety, the development of regulatory standards, and public awareness and acceptance of the use of nanotechnology in the food industry will also come to the forefront.

Concluding Remarks

Nanotechnology is becoming increasingly important in food packaging. The incorporation of nanomaterials into food packaging improves the mechanical, thermal, and barrier properties of packaging materials. One of the problems in the food industry is the time-consuming nature of quality-control analysis. The development of nanosensors to detect microorganisms and gases and the use of nanoscale enzyme immobilization systems are promising applications of food nanotechnology. However, despite the widespread use of nanocomposites in food

Table 5 Some regulations stated on food nanotechnology

Year	Organization/directive	Regulation	References
2004	European Commission/Regulation on Materials and Articles Intended for Food Contact (EC, No 1935/2004)	The Regulation on Materials and Articles Intended for Food Contact, (EC) No 1935/2004, regulates food packaging including new types of materials which actively maintain or improve the condition of the food (active FCMs), which is widely viewed as a promising use of nanomaterials	[147]
2008	Food Additives Directive (89/109/EEC)	It was the first piece of legislation to mention nanotechnologies explicitly. Article 12 of this document states that if there is a change in the starting material used or in the production method of an additive (for example, a change of the particle size), it must undergo a new authorization process and safety evaluation	[60]
2009	Active and Intelligent Materials and Articles Intended to Come in Contact with Food (EC) No 450/2009	It is stated that if legislation limits the quantity of a substance in a food, the total quantity should not exceed this limit regardless of the source, i.e. originally included in the foodstuff or following release of that substance from the FCM. If a substance is released into the food in this way, it is required to be included in the ingredients list For active food substances that are not designed to be released from the packaging and have no function in the food, there is a risk that these substances may migrate into the food. The approach with these types of materials is the same as for plastic materials, which is that these substances should undergo a safety assessment by European Food Safety Authority (EFSA) and a Community authorization. Once authorized, the substance can be placed on a positive list and used within specific constraints	
2010	Novel Food Regulation/(EC) No 258/97	In the Novel Food Regulation ((EC) No 258/97), novel foods are defined as “foods and food ingredients that have not been used for human consumption to a significant degree within the Community” (European Commission, [35]. Under this Regulation, foods deemed to be novel must undergo a safety assessment prior to being placed on the market. It is thought that the soon to be revised Novel Food Regulation ((EC) No 258/97) will be more specific in terms of nanotechnologies than previous documents	[35]
2011	National Industrial Chemicals Notification and Assessment Scheme (NICNAS)	NICNAS, which regulates chemicals for the protection of human health and the environment, has recently introduced new administrative processes to address nanotechnology. NICNAS determines volumes, types, and data holdings of nanomaterials being used in Australia, and has the responsibility of determining whether legislation is sufficient to protect people from potential risks arising from nanotechnology	[119]

packaging, considerable research has not yet been done on the safety of nanocomposite materials. Experimental tests are needed to ensure the safety of such packaging materials. In the case of migration phenomenon, it is important to know that the contact solution could significantly affect the polymer structure and exacerbate the migration of contaminants. On the other hand, nanoparticles that incorporate in the packaging structure are almost minerals, and their diffusion process in non-polar matrix of polymers is unknown. Therefore, experimental study on the migration of nanoparticles seems to be necessary. In relation to platelet-like nanoparticles, knowing the type of morphology (intercalation/exfoliation) is important to better judge the migration mechanisms of nanoparticles.

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