

Review of Mechanical Properties, Migration, and Potential Applications in Active Food Packaging Systems Containing Nanoclays and Nanosilver

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Abstract: The incorporation of nanomaterials into a range of polymeric materials shows great potential for developing new active food packaging systems. Although there are many suggested benefits of nanoparticles (NPs) in food packaging, there are also potential risks due to the possibility of such particles migrating into foodstuffs. This has obvious implications for human health and it may also negatively impact on marketing and consumer confidence. This review focuses on 2 particular types of nanomaterials: nanoclays and nanosilver, with a view to examining the effects of these on system mechanical properties (nanoclays) and antimicrobial efficacy (nanosilver). It further reports on the various migration studies, techniques for characterization, and measurement of NPs as well as the potential migration of NPs from packaging into foodstuffs. Assessment of the literature to date suggests there is an urgent need for further research in order to devise better NP detection methods and to determine the likelihood of their migration from packaging materials into foodstuffs.

Keywords: antimicrobial, active packaging, food packaging, nanoparticles, nanotechnology

Introduction

The rapid growth of nanotechnology in materials science holds great potential for a wide range of industries. This includes the food sector with benefits expected in food safety and quality, the delivery of micronutrients and bioactive ingredients, as well as in food processing and packaging (Chaudhry and others 2008; Han and others 2011). With regard to the latter, previous studies have demonstrated that packaging materials that incorporate nanoparticles (NPs) have the potential to be useful in active food packaging applications (Chaudhry and Castle 2011; Han and others 2011; Abdollahi and others 2012). In this regard, the selection of appropriate polymeric materials is important in developing such systems. The addition of nanomaterials such as nanoclays, carbon nanotubes, and silica NPs can potentially expand the use of such polymeric materials, and their addition to polymers has been related to improvements in overall performance including enhanced mechanical, thermal, and barrier properties (Rhim 2011). In addition, nanomaterials can potentially expand the use of bio-based films (Sorrentino and others 2007; Duncan 2011; Cushen and others 2013).

Active packaging (AP) technologies are designed primarily with the goal of protecting food products from deterioration

and from the growth of microorganisms (Juneja and Sofos 2005; Dainelli and others 2008). In general, AP technologies can be divided into 3 categories: absorbing systems; releasing systems; and other specialty systems for temperature, ultraviolet light, and microwave control (Ahvenainen 2003). Common examples of the 3 forms of AP systems include oxygen scavengers, carbon dioxide scavengers/emitters, moisture absorbers, ethylene scavengers/absorbers, ethanol emitters, and antimicrobial (AM) systems (Hotchkiss 1997; Vermeiren and others 1999; Appendini and Hotchkiss 2002). AP materials that release active compounds for enhancing the quality and safety of a wide range of foods during extended storage are particularly important (Ranjan and others 2014). Many forms of AP technologies involve the use of films produced from polymeric materials that act as carriers (or matrices) for different active substances. These include AM agents where it is necessary to maintain a sufficient concentration of the agent on the food surface in order to control or inhibit the growth of spoilage and pathogenic microorganisms on the food product (de Azeredo 2013). Although, there are currently only a limited number of commercially produced packaging materials that incorporate NPs, there is an increasing recognition of the potential use of NPs in AM packaging systems for the preservation of food products against microbial contamination and for the extension of the shelf-life of the packaged products (Busolo and others 2010). Several researchers have investigated the potential use of nanosilver in AM packaging systems against various microorganisms, particularly on agar-based and liquid culture media and on actual foodstuffs (Emamifar and others 2010b; Kanmani and Rhim 2014b; Ni and others 2014; Sadeghnejad and others 2014).

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In the present review, active food packaging systems containing specifically nanoclays or nanosilver agents are considered in terms of the three important aspects to be taken into account when designing modern food packaging materials. These are: (i) the effect of any system additive or agent on the physicochemical properties of the substrate polymer, (ii) the release of the active agent and hence the effectiveness of the system as an AP technology and, (iii) the range of possible applications of the technology to the packaging of real food products.

The review therefore includes an overview of AM activity imparted by the 2 selected types of NPs incorporated into a range of polymeric materials that are commonly used for food packaging applications and provides a detailed summary of studies relating to the migration of the NPs into the various polymeric substrates. In relation to the physicochemical properties of nanocomposite materials, the review focuses primarily on bio-based food packaging polymeric substrates containing nanoclays in particular as these systems are becoming of increasing importance because of their decreased environmental footprint compared to the traditional synthetic materials. A detailed investigation of the effect of NPs on the specific barrier, physical, thermal, and optical properties of the food packaging system is beyond the scope of this review.

Mechanical Properties of Nanoclay Composites Used in Food Packaging Applications

Overview of food packaging composites containing nanoclays

Packaging materials with adapted mechanical properties that are prepared from petroleum-based synthetic polymers combined with nanoclays and/or other nanomaterials have recently attracted great attention in the food and packaging industries. These nanocomposites have a wide range of potential applications including the nanoencapsulation of nutrients as well as AM food-packaging systems (Chaudhry and Castle 2011; Han and others 2011). The ultimate properties of nanocomposites are influenced by the nature, properties, and content of the individual forms of the nanoclays and/or other components (Sothornvit and others 2010), the physical dimensions of the components (Alexandre and Dubois 2000), and the interfacial interactions between the polymer matrix and the dispersed phase (Hussain and others 2006). Nanoclays in particular have attracted recent interest with a particular focus on their incorporation into various polymers to produce nanocomposites (Majeed and others 2013). Montmorillonite (MMT) is among the most commonly used layered silicates used to form nanocomposites because it is readily available in large quantities and at a relatively low cost (Chaudhry and others 2008; Cyras and others 2008).

MMT is a hydrated alumina-silicate layered clay consisting of an edge-shared octahedral sheet of aluminum hydroxide between two silica tetrahedral layers (Weiss and others 2006). Such nanoclay additives that are incorporated into and/or coated onto polymer packaging film may improve the mechanical properties of the resulting material. Thus, various forms of nanoclays, including MMT, Na^+ -MMT, Cloisite- Na^+ , Cloisite 30B, and Cloisite 20A, can be incorporated into packaging films to improve the performance of various polymers such as: polyamide (PA) or nylon (Wu and others 2002; Mohanty and Nayak 2007; Pereira and others 2009), low-density polyethylene (LDPE) (Zhao and others 2012), polystyrene (PS), poly(lactic acid) (PLA) (Molinaro and others 2013), ethylene-vinylacetate (EVA) copolymer, epoxy resins, polyurethane, and polyethylene terephthalate (PET)

(Parvinzadeh and others 2010) as well as chitosan (Abdollahi and others 2012). The changes in the properties of the resultant film include improvement of mechanical properties, thermal stability, and water vapor permeability (WVP). The observed improvement of properties in the latter may be attributed to the high surface area of the NPs (Uyama and others 2003; Majeed and others 2013).

Mechanical properties of food packaging polymers containing nanosilver

Nanosilver is well known for its broad spectrum antibacterial properties and as such, it has been widely incorporated into a range of packaging materials (Emamifar and others 2010b; Guo and others 2013; Kanmani and Rhim 2014b; Ni and others 2014; Sadeghnejad and others 2014). Although the primary goal of incorporating nanosilver into packaging films is to impart AM activity and improve food safety, there are some additional benefits that can be gained from this additive. For example, poly(hydroxyalkanoate) (PHA) biopolymers incorporated with a combination of nanosilver and cellulose nanocrystals show improved mechanical strength compared with the unfilled PHA (Yu and others 2014). Other systems involving PLA incorporated with microcrystalline cellulose (MCC) and nanosilver show a positive reinforcement is obtained although this is attributed to the MCC with the nanosilver imparting antibacterial activity (Fortunati and others 2012a; Fortunati and others 2012b).

Chitosan films have shown an increase in tensile strength (TS) and a concurrent decrease in elongation at break (EB) by approximately 10% and 15% respectively with the inclusion of 5% (w/w) nanosilver (Rhim and others 2006). A recent study of multifunctional chitosan nanocomposite films containing silver supported MMT reports improved barrier and mechanical strength with the addition of the NPs (Lavorgna and others 2014). Other bio-based films such as poly(L-lactide) have shown no changes in mechanical properties with the addition of up to 1% (w/w) nanosilver (Martinez-Abad and others 2014).

Petroleum-derived materials have also been incorporated with nanosilver to impart AM activity with films of LDPE, for example, reported to show no changes in mechanical strength with the addition of nanosilver at relatively low concentrations (Jokar and others 2012). It was suggested that weakening of the mechanical properties may occur at higher nanosilver concentrations but only relatively low concentrations are usually required to impart effective AM activity. Other LDPE films containing nanosilver have been reported to show reduced EB with increasing nanosilver contents (Emamifar and others 2010a). Polyethylene (PE) films containing nanosilver up to 1% (w/w) show similar mechanical properties to unfilled PE films with this level of nanosilver able to impart significant AM activity (Aalaie and others 2011). Another example of composite films comprised of linear LDPE (LLDPE) with nanoclay and nanosilver showed improved mechanical strength as well as better barrier and AM properties compared with the neat LLDPE film (Jain and others 2008).

Mechanical properties of bio-based food packaging systems containing nanoclay

Nanocomposite materials with suitable mechanical properties can also be prepared from bio-based materials including polysaccharides and protein-based materials (Rhim and others 2006; Sorrentino and others 2007; Sothornvit and others 2009). For example, nanoclays can be effectively integrated into bio-based polymers such as starch-based films (Cyras and others 2008; Heydari and others 2013), cellulose-based films (Mahmoudian

and others 2012; Kanmani and Rhim 2014a), agar-based films (Rhim 2011), and protein-based polymers such as soy protein (SP) (Kumar and others 2010), soy protein isolate (SPI) (Echeverría and others 2014), and whey protein isolate (WPI) (Sothornvit and others 2009, 2010). Such nanocomposites have improved mechanical properties that may see them being applied more widely in the future for various food packaging applications (Müller and others 2011; Zhang and Wang 2012). Studies on the effects of nanoclays on the mechanical properties of packaging materials are summarized in Table 1.

As shown in Table 1, nanoclays can be effectively combined with starch-based polymers, and the resultant films are emerging as one of the more promising forms of AM packaging systems because of the improvement in mechanical properties. Such claims of improvement in properties include a recent study conducted by Heydari and others (2013) who investigated the effect of Na^+ -MMT on the mechanical properties of corn starch films. It was reported that the addition of 2.5% (w/w) Na^+ -MMT decreased the percentage EB by about 20%, increased the TS by about 12%, and more than doubled the Young's modulus (YM) compared with the control film. In another study, Cyras and others (2008) studied the effects of MMT on the physicochemical properties of starch-based films. They reported that the addition of 5% (w/w) MMT increased the TS, decreased the EB by 15.8%, and significantly increased the YM more than 6-fold compared with the control.

Dean and others (2007) developed starch nanocomposite films containing Na^+ -MMT and examined the effects of the additive on the mechanical performance of the film. The authors claimed a significant improvement in the modulus and TS, whereas the EB decreased compared with the control film. Avella and others (2005) reported that the addition of MMT to thermoplastic starch (TPS) resulted in an approximate 107% increase in the YM compared with the control film and decreased the EB by 15%, but there was no discernible effect observed for the TS of the unconditioned films. However, the authors observed increases in the TS, EB, and YM at 15% relative humidity (RH), but only increases in TS and YM at 60% RH.

Huang and others (2004) investigated the properties of TPS nanocomposites incorporated with MMT and found an improvement in the mechanical properties of the films. Furthermore, Chen and Evans (2005) observed an increase in the YM of TPS/MMT films. Park and others (2003) showed that Cloisite- Na^+ and Cloisite 30B impregnated into TPS films improved the WVP of the films. They claimed that both forms of nanoclay increased the TS, and the EB decreased slightly with the incorporation of Cloisite 30B, but the opposite was observed for the EB of TPS films impregnated with Cloisite- Na^+ .

Table 1 also summarizes the effects of various forms of nanomaterials such as Cloisite- Na^+ , Cloisite 30B, and Cloisite 20A incorporated into PLA on the properties of this substrate as determined by different researchers. Rhim and others (2009) investigated the effect of these nanoclays incorporated into PLA film on the resulting mechanical properties. They reported that the addition of Cloisite- Na^+ and Cloisite 30B reduced the TS by about 19%, whereas the addition of Cloisite 20A into PLA film resulted in a TS reduction of 10%. They also reported that Cloisite- Na^+ and Cloisite 20A slightly decreased the EB, whereas Cloisite 30B slightly increased the EB of PLA. Moreover, Fukushima and others (2011) incorporated 5% (w/w) fumed silica into PLA and reported a significant improvement in the mechanical properties of the resultant films.

Nanoclays and/or other NPs can also be incorporated into polysaccharide-based polymers such as agar films. These materials generally demonstrate good film-forming properties and previous studies have shown that the introduction of nanoclays into agar-based films can improve the physicomechanical properties, thereby expanding their use into AM food packaging applications. Rhim and others (2011) studied the effects of Cloisite- Na^+ , Cloisite 30B, and Cloisite 20A on the mechanical properties of agar-based films. The addition of Cloisite- Na^+ resulted in a reduction of the TS by 5%, with a slight increase in the EB. However, Cloisite 30B and Cloisite 20A increased the TS by about 7% and 13%, respectively, and these forms of nanoclay also increased the EB of the films. Kanmani and Rhim (2014a) investigated the effect of ZnO on the mechanical properties of agar and carrageenan films. The TS of both films decreased with the addition of ZnO, whereas the EB of the agar film increased by 30.7% and that of carrageenan film increased by 17.9%. The authors also reported that ZnO decreased the YM of agar and carrageenan films.

Interest in the potential applications of NPs such as nanoclays in the chitosan polymers for use in food packaging applications has increased over the past decade. Chitosan polymers demonstrate adequate film-forming properties when impregnated with various nanomaterials (Xu and others 2006). For example, Rhim and others (2006) developed chitosan films containing 5% (w/w) Na^+ -MMT, Cloisite 30B, and nanosilver and studied the impacts of these additives on the mechanical properties of the films. The authors claimed an increase in the TS by about 7%, 12%, and 9% for each of these additives respectively. They also reported that Na^+ -MMT and nanosilver decreased the EB of chitosan films, whereas Cloisite 30B increased the EB. In agreement with these findings is the work of Casariego and others (2009) who observed that the incorporation of nanoclay into chitosan film improved the overall performance of the film with an observed increase of the TS values. Abdollahi and others (2012) incorporated MMT into chitosan films and showed that the TS was increased with a decrease in the EB value. Xu and others (2006) investigated the effects of MMT- Na^+ and Cloisite 30B impregnated into chitosan films and found that these nanoclays increased the TS of the films, whereas the EB of the film decreased.

Protein-based films exhibit improved gas barrier properties when impregnated with nanomaterials, and nanoclays in particular (Zhao and others 2008). Various forms of protein-based polymers such as wheat gluten, SP, and SPI, among many others, have the potential to be developed into AP materials for food packaging applications. Table 1 demonstrates the successful incorporation of NPs into a range of protein-based films that have shown considerable potential for food packaging applications. For example, Tunc and others (2007) developed a nanocomposite film based on wheat gluten incorporated with Na^+ -MMT. They reported that the incorporation of 2.5% (w/w) Na^+ -MMT into these systems increased the TS and YM of the film compared with the control film. However, the addition of Na^+ -MMT at the same concentration slightly decreased the EB of the wheat gluten film. Kumar and others (2010) studied the effects of MMT on the properties of SPI film. Their results suggested that SPI film containing 5% (w/w) MMT exhibited an increased TS and EB. Echeverría and others (2014) examined the physicomechanical properties of SP film containing 5% (w/w) MMT. The SPI film prepared with 5% (w/w) MMT demonstrated a decrease in TS compared with a control film. These researchers also found that the incorporation of the MMT resulted in a reduction in the EB by about 29% compared with the control film.

Table 1—Effect of nanoclays and other nanomaterials on the mechanical properties of packaging materials.

Packaging	Nanomaterial	Loading % (w/w)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Reference
PLA	Cloisite Na ⁺ Cloisite 30B	5	Decrease: 50.5 to 40.8	Increase: 2.5 to 3.0	Rhim and others (2009)	
			Decrease: 50.5 to 40.9	Slight increase: 3.0 to 3.1		
Agar-based film	Cloisite 20A Cloisite Na ⁺ Cloisite 30B	5	Decrease: 50.5 to 45.3	Slight decrease but not significant	Rhim and others (2011)	
			Decrease: 70.3 to 67.0	Increase: 45.3 to 49.8		
Agar film	Cloisite 20A	1.5	Significant increase: 70.3 to 79.2	Significant increase: 45.3 to 57.4	Kanmani and Rhim (2014b)	
			Decrease: 34.6 to 13.0	Increase: 25.6 to 56.3		
CMC	ZnO		Decrease: 6.4 to 5.1	Increase: 68.7 to 72.9	Decrease: 20.5 to 14.0	Rhim and others (2011)
Carrageenan film			Decrease: 44.6 to 12.3	Increase: 24.2 to 42.1	Decrease: 1004.9 to 109.8	
WPI film	Cloisite Na ⁺ Cloisite 20A	5	Decrease: 3.40 to 2.98	Decrease: 50.9 to 42.4	Decrease: 1112.1 to 130.4	Sothornvit and others (2009)
			Decrease: 3.40 to 1.55	Significant decrease: 50.9 to 29.1	Decrease: 171.8 to 109.3	
SPI	Cloisite 30B	5	Decrease: 3.40 to 3.29	Slight increase: 50.9 to 51.7	Decrease: 171.8 to 115.5	Kumar and others (2010)
			Increase: 2.26 to 6.28	Significant increase: 11.85 to 64.6	Decrease: 171.8 to 162.6	
SP	MMT	5	Increase: 3 to 5.2	Decrease: 38 to 27	Increase: 26 to 34.6	Echeverría and others (2014)
Gelatin	Cloisite 20A	18	Decrease: 22 to 16	Decrease: 21 to 15.8	Increase: 3300 to 8300	
Gelidium corneum	Cloisite Na ⁺ Cloisite 30B	3	Increase: 19.5 to 27.3	Increase: 15 to 24	Rao (2007)	
			Increase: 19.5 to 26.40	Increase: 15 to 33		
Gelatin	Cloisite Na ⁺ Cloisite 30B	10	Increase: 88.9 to 110.8	Significant decrease: 9.6 to 0.9	Jang and others (2010)	
			Increase: 26.65 to 38.13	Decrease: 76.35 to 55.20		
Gelidium corneum-gelatin	Cloisite Na ⁺ Cloisite 30B	1	Increase: 26.65 to 37.62	Decrease: 76.35 to 57.96	Tunc and others (2007)	
			Increase: 26.65 to 32.82	Decrease: 76.35 to 59.68		
Wheat gluten films	Na ⁺ -MMT	2.5	Increase: 1.86 to 2.37	Slight decrease: 58.4 to 55.4	Xu and others (2006)	
			Increase: 1.86 to 4.70	Slight decrease: 58.4 to 16.0		
Chitosan film	MMT-Na ⁺	7.5	Increase: 1.86 to 3.60	Decrease: 58.4 to 15.2	Abdollahi and others (2012)	
			Increase: 40.62 to 54.98	Decrease: 13.14 to 8.72		
Chitosan	Na ⁺ -MMT	5	Increase: 40.62 to 65.67	Decrease: 13.14 to 10.81	Casariego and others (2009)	
			Increase: 40.62 to 44.51	Decrease: 13.14 to 8.98		
Chitosan	Cloisite 30B	5	Increase: 40.62 to 45.01	Increase: 13.14 to 14.40	Rhim and others (2006)	
			Increase: 40.62 to 47.97	Decrease: 13.14 to 5.71		
Starch	MMT	5	Increase: 40.62 to 47.29	Decrease: 13.14 to 4.42	Cyran and others (2008)	
			Increase: 60.8 to 69.33	Decrease: 3.79 to 3.01		
Starch film	Clay NPs	1	Increase: 11 to 22	Decrease: 1.4 to 6	Dean and others (2007)	
			Increase: 32.9 to 35.1	Decrease: 54.6 to 50.3		
Starch	Na ⁺ -MMT	5	Increase: 32.9 to 36.8	Increase: 54.6 to 66.3	Huang and others (2004)	
			Increase: 32.9 to 35.9	Decrease: 54.6 to 46.3		
Starch	Nano-silver	5	Increase: 3.3 to 5.2	Decrease: 62.6 to 46.8	Avela and others (2005)	
			Increase: 3.3 to 5.2	Decrease: 62.6 to 46.8		
Starch	MMT	3.2	Increase: 3.3 to 5.2	Decreased	Park and others (2003)	
			Increase: 3.3 to 5.2	Decreased		
Starch film	Na ⁺ -MMT	30	Increase: 5.5 to 27.3	Decrease: 85.3 to 17.8	Heydari and others (2013)	
			Increase: 5.5 to 27.3	Decrease: 85.3 to 17.8		
Starch	MMT	4	No discernible change observed	Decrease: 25 to 10	Chen and Evans (2005)	
			Increase: 2.6 to 3.3	Increase: 47 to 57		
Starch	Cloisite Na ⁺ Cloisite 30B	5	Increase: 2.6 to 2.8	Decrease: 47 to 44	Park and others (2003)	
			Increase: 7.30 to 8.14	Decrease: 45.96 to 36.85		
Starch	Na ⁺ -MMT	5	Increase: 7.30 to 8.51	Increase: 45.96 to 49.18	Heydari and others (2013)	
			Increase: 7.30 to 8.51	Increase: 45.96 to 49.18		
TPS films	MMT	5	Increase: 2.61 to 2.79	Slight increase: 47.0 to 48.9	Chen and Evans (2005)	
			Increase: 2.61 to 3.32	Increase: 47.0 to 57.2		
TPS films	Cloisite Na ⁺	2.5	Increase: 2.61 to 3.32	Increase: 47.0 to 57.2	Park and others (2003)	
			Increase: 2.61 to 3.20	Increase: 47.0 to 52.0		
Cloisite 30B	Cloisite 30B	10	Increase: 2.61 to 2.75	Slight decrease: 47.0 to 45.7	Chen and Evans (2005)	
			Increase: 2.61 to 2.75	Slight decrease: 47.0 to 45.7		
Cloisite 30B	Cloisite 30B	5	Increase: 2.61 to 2.80	Decrease: 47.0 to 44.5	Park and others (2003)	
			Increase: 2.61 to 3.00	Decrease: 47.0 to 45.7		
Cloisite 30B	Cloisite 30B	10	Increase: 2.61 to 3.00	Decrease: 47.0 to 45.7	Park and others (2003)	
			Increase: 2.61 to 3.00	Decrease: 47.0 to 45.7		

Gelidium corneum (GC) is a type of red alga containing the highly linear polysaccharide agarose that is widely used in processed food, culture media, and pharmaceutical applications (Hong and others 2009). Films that are comprised of GC require improvement in their physical properties because of their inherently weak TS and poor EB characteristics. Consequently, a GC-gelatin (GCG) blend film has been considered as a way to improve the physical properties of GC because gelatin has an excellent film-forming ability and good physical properties (Cao and others 2007). Jang and others (2010) investigated the effect of Cloisite- Na^+ on the mechanical properties of GCG film. The authors reported that 1% (w/w) of the additive increased the TS of the film and caused a decrease in the EB compared to the control film and this effect is amplified when the concentration is increased from 3% to 5% (w/w). Recently, Farahnaky and others (2014) investigated the mechanical properties of gelatin-clay nanocomposites and claimed that the TS and YM increased with an increase in the concentration of the clay, whereas the EB decreased. Lim and others (2010) developed GC films incorporated with 3% (w/w) Cloisite- Na^+ and Cloisite 30B and studied the effects of these nanoclays on the mechanical properties of the resultant films. They reported that the TS of the films were about 29% and 26% greater than the control films when incorporated with Cloisite- Na^+ and Cloisite 30B, respectively. The authors also claimed that the addition of the nanoclays reduced the EB of the films. Rao (2007) found that Cloisite- Na^+ incorporated into gelatin films increased the YM and TS, but the EB decreased with higher Cloisite- Na^+ content compared with the control films.

The findings summarized in Table 1 underscore the potential of incorporating nanoclays into various polymers to form nanocomposites that can be used for food packaging applications. In general, the inclusion of various forms of nanoclay into polymeric materials decreases the EB of the resultant films, suggesting a reduction in the overall elasticity of the composites as a result of the presence of the nanomaterial. Conversely, the TS and YM tend to increase, suggesting that reinforcement occurs upon the addition of the nanomaterial. In contrast, Sothornvit and others (2009) reported a decrease in the YM for WPI composite incorporated with Cloisite 20A and Cloisite 30B, although most other examples in Table 1 report increases in the same property. Although there is clearly a strong potential for improvements in mechanical properties of various packaging films, the effects of the concentration of the nanoclay is yet to be investigated as some forms of nanoclay at higher concentrations might have detrimental effects on the properties of the films.

Migration of Nanoclays and Nanosilver from Active Food Packaging Materials

The release of NPs can play an important role in determining the activity of the packaging material as well as in the inhibitory effect the packaging has on the spectrum of microorganisms (Fernández and others 2010; Huang and others 2011; Cushen and others 2013; Fortunati and others 2013). LaCoste and others (2005) suggested that the design of an AM packaging system requires knowledge of controlled release technology and microbial growth kinetics since the release system involves the migration of the AM agent into the food or the headspace inside the package to inhibit the growth of microorganisms (Sung and others 2013). The release kinetics of a packaging system is generally studied by measuring the release rate of the AM agent into a food simulant or by measuring its effectiveness in inhibiting microbial growth and extending the shelf-life of the product (Ahvenainen 2003; Brody and others

2008). Adequate control of the release and migration of AM agents from the food packaging is very important in order to sustain AM activity over an extended period (Han 2003; LaCoste and others 2005).

Factors affecting the mass transfer characteristics of an AM substance include its AM activity and the mechanism and kinetics of the selected substance in targeting microorganisms (Han 2000; Brody and others 2008; Sung and others 2013). Furthermore, the release kinetics should be designed to control the growth of the microbes and maintain the AM concentration above the critical inhibitory concentration (Han 2000). Little has been reported on the potential migration of nanoclays incorporated or coated onto polymeric materials into food simulants.

Migration of nanoclays

Although there are many potential benefits for the application of nanoclays in AP technologies, there is limited information about the possible risks associated with these migrating from the packaging material into the foodstuff and, hence, the possible risk to human health. Table 2 summarizes the studies that have investigated the possible migration of nanoclays from packaging materials into various food simulants. For example, Fahoodi and others (2014) determined the migration of nanoclay (Cloisite 20A) incorporated into PET films as well as the effects of temperature on the migration. They found that the migration of aluminum and silicon from PET films into 3% (w/v) acetic acid is dependent on storage time and temperature. Their results also suggest that the concentrations of aluminum in the simulant after 90 d storage at 25 and 45 °C increased by 1.8-fold. The silica concentrations in the simulant increased by 58% after the same storage times at 25 and 45 °C, however, the authors did not address whether the migrated aluminum and silicon were present as ionic species or NPs.

In their studies, Avella and others (2005) detected low levels of MMT constituents (magnesium, iron, and silicon) that had migrated from starch/clay nanocomposite films into vegetables (lettuce and spinach). They also reported low-level migration of these elements from packaging into distilled water as a food simulant. In agreement with this study, Mauricio-Iglesias and others (2010) reported low levels of MMT migration from wheat gluten/MMT films into food simulants. Schmidt and others (2009) also reported relatively low levels of migration of Cloisite 30B from PLA into 95% (v/v) ethanol when stored at 40 °C for 10 d. In another study by these researchers, the migration of modified magnesium-aluminum layered double hydroxides (LDHs) into food simulants from PLA films was reported. Using inductively coupled plasma mass spectrometry (ICP-MS), the authors found relatively low total migration of LDH platelets from the nanocomposite films (Schmidt and others 2011).

Migration of nanosilver

Although the number of commercial packaging materials incorporating nanosilver is currently limited, more recently there has been an increased recognition of the potential use of nanosilver in AM packaging systems (Emamifar and others 2010b; Kanmani and Rhim 2014b; Ni and others 2014; Sadeghnejad and others 2014). A major concern that has been identified by these and other researchers is the potential for nanosilver or silver ions to migrate from the packaging onto food products where it can be ingested by consumers (Agarwal and others 2013; Gaillet and Rouanet 2014). Several recent reviews in this area have been published and these highlight a number of critical issues including the measurement

Table 2–Studies on the migration of nanoparticles from food packaging materials.

Packaging material	Nanoparticle/nanomaterial	Loading	Application	Technique	Time to equilibrium (d)	Simulant/food	Test temperature (°C)	Equilibrium migration quantity	Reference
PE	Ag	100 µg/g	AM	AAS	15	Water	25	1.3 µg/dm ²	Huang and others (2011)
							40	3.3	
							50	3.5	
							25	1.7	
							40	3.4	
							50	3.7	
							25	0.9	
							40	2.6	
							50	3.1	
							40	1.6	
40	3.6								
50	4.1								
Starch-based film	MMT	4% (w/w)	Food packaging	AAS	10	Lettuce	40	Fe: 2.2 mg/100 g, Mg: 45.7, Si: 0.28	Avella and others (2005)
							Spinach	Fe: 3.3 mg/100 g, Mg: 55.2, Si: 0.3	
PLA	Ag-nanoclay	1% (w/w) 5% 10%	AM	Stripping voltammetry	8	0.03% (v/v) HNO ₃	RT	4.2 mg/kg 6.1	Busolo and others (2010)
PET	Cloisite 20A	3% (w/w)	Migration	ICP-OES	90	3% (w/v) acetic acid	25	Al: 0.18 mg/kg, Si: 6.0	Fahoodi and others (2014)
PVC	Ag	0.5% (w/w)	Migration	ICP-MS	2	Chicken breast	19.94	0.01 mg/dm ²	Cushen and others (2013)
					4		0.27		
					2		0.43		
PLA	Ag	1% (w/w)	Migration	ICP-MS	10	10% (v/v) ethanol	40	4.0 µg/kg	Fortunati and others (2013b)
					2	Isooctane	20	4.0 µg/kg	
LDPE	Ag	2 × 10 ⁴ ng/cm ²	AM	ICP-MS	2 h	50% (v/v) ethanol	70	<4.07 ng/mL	Echegoyen and Neri (2013)
					10 h	3% (v/v) acetic acid	40	0.003 ng/cm ²	
PP	Ag	39 × 10 ⁴ ng/cm ²	AM	ICP-MS	2 h	50% (v/v) ethanol	70	1.66 ng/cm ²	
					19 × 10 ⁴	3% acetic acid	<1.06 ng/mL		
					39 × 10 ⁴ ng/cm ²	50% (v/v) ethanol	0.018 ng/cm ²		
		19 × 10 ⁴			10 h	3% (v/v) acetic acid	40	<4.07 ng/mL	
		19 × 10 ⁴			10 h	50% (v/v) ethanol	40	0.018 ng/cm ²	
		19 × 10 ⁴			10 h	3% acetic acid	40	9.48 ng/cm ²	
		19 × 10 ⁴			10 h	50% (v/v) ethanol	40	31.46	
		19 × 10 ⁴			10 h	3% (v/v) acetic acid	40	7.10	
		19 × 10 ⁴			10 h	50% (v/v) ethanol	40	10.16	

(Continued)

Table 2–Continued

Packaging material	Nanoparticle/nanomaterial	Loading	Application	Technique	Time to equilibrium (d)	Simulant/food	Test temperature (°C)	Equilibrium migration quantity	Reference
PLA	LDH	5.5% (w/w)	Migration	ICP-MS	10	3% (v/v) acetic acid	40	0.018 ng/cm ²	Schmidt and others (2011)
PLA	Cloisite 30B	5% (w/w)	Migration	AFHF-MALS-ICP-MS	10	95% (v/v) ethanol	40	6.7 mg/dm ²	Schmidt and others (2009)
PE	Ag	0.5% (w/w)	Migration	ICP-MS	1.1	Chicken breast	8.13 21.8	0.003 mg/dm ² 0.004	Cushen and others (2014)
					3.1		8.13	0.005	
					1.1		21.8	0.004	
					3.1		8.13	0.032	
					3.1		21.8	0.044	
					3.1		8.13	0.024	
					3.1		21.8	0.049	
LDPE	Ag	10% (w/w)	AM		10	10% (v/v) ethanol	40	<0.001 ppm	Panea and others (2014)
	ZnO							2.44 ± 0.37 ppm	
PE	Ag	28 µg/g	AM, migration	AFHF-ICP-MS	10	Distilled water	20	10 ± 2 ng/L	Artiaga and others (2015)
					0.08	3% (w/v) acetic acid	20	34 ± 8	
						10% (v/v) ethanol	20	Not detectable	
						95% ethanol	40	Not detectable	
						Distilled water	40	18 ng/L	
						3% (w/v) acetic acid	70	9	
						Distilled water	70	17	
						3% (w/v) acetic acid	20	17	
PP	Ag	11.9 µg/g	Migration	SN-ICP-MS	10	3% (w/v) acetic acid	20	9.5 ng/cm ²	Von Goetz and others (2013)
						10% (v/v) ethanol		4.75	
						Distilled water		4.75	
						Olive oil		> 1.0 ng/g	
PE	Ag	234 mg/kg	Migration	ICP-MS	9 h	3% (w/v) acetic acid	20	3.98 mg/kg	Song and others (2011)
							40	7.02	
							70	13.10	
							20	0.562	
							40	0.5382	
							70	0.5148	

of the toxicity and release of silver and nanosilver (Duncan 2011; Nelson and others 2011; Reidy and others 2013; Trbojevich and Fernandez 2013; Gaillet and Rouanet 2014), regulatory and other safety issues (Faunce and Watal 2010; Dos Santos and others 2014), and other environmental concerns (Massarsky and others 2014). It is evident from these reviews that the application of silver and nanosilver must be justified by a risk-benefit analysis to consumers and that the incorporation of these materials should be regulated to avoid overuse (Reidy and others 2013).

The migration of silver and nanosilver from packaging materials such as PE, LDPE, polypropylene (PP), poly(vinyl chloride) (PVC), and PLA films has been the subject of several studies that are summarized in Table 2. In particular, these studies have investigated the release of the NPs from polymeric films into food simulants; principally into distilled water, 3% (v/v) acetic acid, 95% (v/v) ethanol, 10% (v/v) ethanol, and isooctane under various experimental conditions (temperature and exposure duration). Some of the studies given in Table 2 have also investigated the release of silver NPs onto the surface of foodstuffs. In one example, a study by Huang and others (2011) determined the migration of nanosilver in commercial PE containers into various food simulants. The authors claimed that nanosilver was released into all the food simulants from the containers and observed that the amount of nanosilver that had migrated into the simulants increased with temperature and storage time. Although this study demonstrated the potential of nanosilver to migrate into all the food simulants during the 15 d of the experiments, two important aspects not considered were: (i) the distinction that can possibly be made between migrated particles and ions within the limitations of the atomic absorption spectroscopy (AAS) technique used in the study and, (ii) the suitability of AAS as an analytical technique for the direct determination of nanomaterial.

More recently, Cushen and others (2014) measured the migration of nanosilver and nanocopper from PE containers onto chicken breast by ICP-MS and reported significantly more copper was released from the containers than silver. Echegoyen and Nerín (2013) studied the release of nanosilver from 3 different PE commercial food containers using various food simulants at relatively high temperatures. After 2 h at 70 °C, silver was detected in 3% (v/v) acetic acid from the different packaging materials, but no silver was detected in 50% (v/v) ethanol. It was also reported that silver migration occurred from all samples into the food simulants for samples stored at 40 °C for 10 d. In a very recent study, Artiaga and others (2015) determined the migration of nanosilver from PE bags using asymmetrical flow field flow fractionation ICP-MS (AFFFF-ICP-MS). Film samples were immersed into a range of food simulants and showed significant silver particle migration occurred into distilled water and 3% (w/v) acetic acid when the samples were stored for 10 d at 20 °C, with no migration being detected into either 10% or 95% (v/v) ethanol. The study clearly demonstrated that the migrating substances are whole NPs rather than ionic species and that AFFFF-ICP-MS is an emerging analytical technique capable of detecting and characterizing NPs.

Song and others (2011) determined the migration of nanosilver incorporated into LDPE films in various simulants after 9 h at 20, 40, and 70 °C. They found that the migration of nanosilver from the films into 3% (w/v) aqueous acetic acid is dependent on storage temperature, whereas for a 95% (v/v) ethanol simulant, the maximum migration ratios were not statistically different after the same storage times at each temperature. Cushen and others (2013) investigated the migration of nanosilver incorporated into PVC films onto chicken breast using ICP-MS, and detected silver

on the substrate after 2 and 4 d of exposure. Fortunati and others (2013) studied the release of silver NPs from PLA film into various food simulants and reported silver migration from the film into 10% (v/v) ethanol after 10 d of storage at 40 °C and into isooctane after 2 d of storage at 20 °C. Since the levels of silver released after 10% (v/v) ethanol and isooctane did not exceed the acceptable migration limits, the authors suggested that PLA films containing silver NPs could be applied as a releasing system for AP technologies.

von Goetz and others (2013) determined the migration of nanosilver in PP containers into a range of food simulants and found that the equilibrium migration into 3% (w/v) acetic acid was twice the amount detected in either distilled water or 10% (v/v) ethanol after exposure at 20 °C for 10 d. However, the migration into olive oil was very low at less than 1.0 ng cm⁻³. It is important to note that this study has clearly distinguished between migrated particles and ions by using ICP-MS in single-particle mode.

Panea and others (2014) studied the release of silver NPs from LDPE film into 10% (v/v) ethanol. They reported that less than 1 ppb silver migrated into the simulant after 10 d of storage at 40 °C. They also found that a higher concentration of ZnO particles was released from LDPE under the same conditions. Busolo and others (2010) investigated the migration of silver-nanoclay incorporated into PLA film immersed in 0.03% (v/v) HNO₃ for 8 d at room temperature. After the storage time, silver-nanoclay was indeed detected in the simulant; however, the use of HNO₃ as a representative food simulant was not adequately addressed.

Analytical techniques and challenges in migration studies

Understanding the behavior of NPs in food and/or environmental samples is difficult because of challenges associated with detecting such small amounts in complex food and/or environmental matrices (Tuoriniemi and others 2012; Proulx and Wilkinson 2014). One particular analytical challenge in NP detection is distinguishing NPs from molecular and/or ionic species (Proulx and Wilkinson 2014). The release of NPs from a packaging material is primarily influenced by the physical and chemical properties of the NPs. This includes their size and size distribution (Šimon and others 2008; Rhim and others 2013), chemical composition including purity, crystallinity, electronic properties (Silva and others 2011), surface properties (area, structure, reactivity, functional groups, inorganic, or organic coatings) (Silva and others 2011), and their solubility, shape, and aggregation (Xu and others 2012). In a theoretical study, Šimon and others (2008) predicted the potential migration of very small NPs from polymer matrices such as LDPE, HDPE, and PP to foods. Verberg and others (2006) mathematically modeled the release of NPs from microcapsules moving within a microchannel. They found that the properties of the microcapsule considerably influenced NP release.

The migration of NPs from packaging materials can also be influenced by the chemical interaction between the NPs and polymer chains, changes in the packaging film that might be induced by the NPs (Sadeghnejad and others 2014), food composition (Mitrano and others 2012), and properties such as pH (Artiaga and others 2015), and migration time and temperature conditions (Song and others 2011). In most cases, it is complicated, time-consuming, and expensive to determine the migration of NPs into real food products because most foodstuffs are heterogeneous mixtures (Lau and Wong 2000; Helmroth and others 2002; Cushen and others 2013). Thus, migration studies on NPs are usually performed using food simulants (Dopico and others 2003),

and different food simulants have been suggested in the European food-packaging regulations for migration testing (European Union 2011). In the United States, examples of food simulants for various food products include: 10% (v/v) ethanol for aqueous and acidic foods; 10% to 50% (v/v) ethanol for low-high alcoholic foods; and food oil or synthetic fat simulant HB 307 for fatty foods (US Food and Drug Administration 2014). In Europe, the list of accepted food simulants includes: 10% (v/v) ethanol, 3% (v/v) acetic acid, or 20% (v/v) ethanol for water based foods; 50% (v/v) ethanol or vegetable oil for fatty foods; and poly(2,6-diphenyl-*p*-phenylene oxide) for dry foods (European Union 2011).

Although considerable research relating to the release of NPs into food simulants is now underway in various research groups, the detection, characterization, and quantification of NPs poses significant challenges (Han and others 2011; Liu and others 2012). There are many analytical techniques that have the potential to be used to detect, quantify, and characterize NPs in food and/or environmental systems. A comprehensive description of these techniques is beyond the scope of this review, but examples include light scattering (Takahashi and others 2008; Brar and Verma 2011), microscopy (Liu and Hurt 2010; Zhang and others 2011), chromatography (Hoque and others 2012; Pergantis and others 2012; Proulx and Wilkinson 2014), and various hyphenated instrumental techniques (Pace and others 2011; Mitrano and others 2012; Lee and others 2014). Nonetheless, some of the important and newly emerging techniques are discussed below. A more comprehensive review of the challenges of measuring the migration of engineered NPs from packaging is given by Noonan and others (2014).

Spectrometric techniques such as single-particle ICP-MS have been applied to the detection of NPs and this technique enables the simultaneous determination of concentration and size (Pace and others 2011; Hagendorfer and others 2012; Tuoriniemi and others 2012; Ulrich and others 2012). However, the most commonly used detection and characterization methods available to assess particle concentration and size distributions are not adequate for the study of NPs in complex systems or at low concentrations (Tiede and others 2008). Indeed, one of the major challenges is that NPs are commonly present at very low concentrations, in the range of ng/L to $\mu\text{g/L}$ but it is claimed that the single-particle ICP-MS technique has the potential to detect, quantify, and size NPs (Lee and others 2014). To do this the ICP-MS instrument is typically operated in a single-particle mode and it is assumed that each pulse represents a single particle event (Pace and others 2011). The frequency of pulses is directly related to the number concentration of particles (number of particles per unit volume), and the intensity of the pulse is related to particle size (Pace and others 2011; Mitrano and others 2012). In single-particle analysis, the smallest peak height that can be distinguished from the background determines the smallest detectable single-particle mass (volume, size); therefore, the detection limit determines the lower particle size threshold of the system (Mitrano and others 2012). The limitations of this technique stem from the sensitivity of the particular ICP-MS instrument being used (Pace and others 2011). Other limitations occur because of the finite temporal resolution of the detector (related to the minimum dwell time) and the finite transfer efficiency between the sample introduction and the detector positions (Pace and others 2011).

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) are techniques that are also widely used to study NPs. Such techniques have the ability to detect single NPs, although this is often difficult to accomplish in practice for nanomaterials in complex matrices, such as food (Mitrano and

others 2012). Although such techniques may provide images of single particles, their shortcomings include unrepresentative sampling, changes during the preparative process and an inability to find particles in very dilute samples (Mühlfeld and others 2007).

Another common technique that has been used in the study of NPs in colloidal solutions is the dynamic light scattering (DLS) technique that measures the particle hydrodynamic diameter (Takahashi and others 2008; Brar and Verma 2011). Limitations for the study of NPs using the DLS technique include poor sensitivity at dilute concentrations, nonselective material detection, failure to differentiate between NPs and other matrix components, and the inability to reliably quantify the relative proportions of particle or aggregate sizes in multi-modal distributions (Hoque and others 2012). Multi-modal populations are particularly problematic for DLS as intensity-normalized results will be characteristically and disproportionately skewed to the larger particles/aggregates in suspension even if smaller sizes predominate (Brar and Verma 2011).

Field flow fractionation (FFF) allows separation and, when combined with appropriate detection systems, subsequent sizing of macromolecules, submicron colloids, and NPs of 1 to 100 nm depending on the type of field applied and mode of operation (Ranville and others 1999; Herrero and others 2014). The separation process is similar to chromatography, except that it is based on physical forces rather than chemical interactions (Fraunhofer and Winter 2004). Particle separation is performed in a thin channel with laminar flow under the influence of a perpendicular field. Depending on the type of analysis that is being performed, a different member of the FFF family is utilized to achieve optimal separation results (Reschiglian and others 2005). The 3 techniques that are the most commercially available and thus most commonly used include thermal, sedimentation, and flow FFF (Messaud and others 2009). Applications of FFF have become increasingly diverse in recent years to include separation and characterization of NPs (Chianéa and others 2000; Bednar and others 2013). Interfacing FFF with ICP-MS or ICP-atomic emission spectroscopy (ICP-AES) allows element-specific detection at trace levels (Dubascoux and others 2010; Poda and others 2011) when studying metal-containing NPs (Gimbert and others 2003). Furthermore, the capability of multi-metal analysis is an added benefit when using these detection techniques (Isaacson and Bouchard 2010). The hyphenated techniques of FFF-ICP-MS and FFF-ICP-AES provide NP detection, sizing, and compositional analysis capabilities at the $\mu\text{g/L}$ level for multiple elements present within the NP (Poda and others 2011; Bednar and others 2013).

Studies and Potential Applications of NPs in Active Food Packaging

New AM packaging systems that belong to the general class of AP systems have attracted much attention in the food industry with the aim of replacing conventional food preservation systems (Cho and others 2011) in which levels of additives in excess of what is required for an efficient AM effect may occur (Kanmani and Rhim 2014b) and lead to adverse organoleptic properties. In AP systems, the product, the packaging, and the environment all interact to extend the shelf-life or to improve microbial safety or sensory properties, while maintaining the quality of the food product (de Azeredo 2013). The shelf-life of the food product is extended by an increase in the lag phase and a consequent reduction in the growth rate of potential spoilage microorganisms (Li and others 2009b; Munro and others 2009; Soares and others 2009). In addition to improving the physicochemical properties

of many polymeric materials, NPs can also be used to create AM packaging systems (Sanchez-Garcia and others 2010) that increase the shelf-life of various foodstuffs (Han and others 2011; Silva and others 2011). Such systems are amongst the more promising forms of AP systems (Sorrentino and others 2007).

In vitro studies involving NPs

The effectiveness of nanoclays and nanosilver in particular as AM agents, and hence their possible use in AP systems, has been demonstrated in the first instance by various *in vitro* experiments. Table 3 lists some of these studies that have evaluated the inhibitory effects of NPs either *in vitro* or directly onto the surfaces of food products. These studies include work conducted by Stanic and others (2010) who investigated the AM activity of ZnO-doped hydroxyapatite against *E. coli*, *S. aureus*, and *C. albicans* and claimed a reduction in the growth of these microorganisms by 1 to 2 log CFU/mL. Hong and Rhim (2008) reported that the organoclays Cloisite 30B and Cloisite 20A show AM activity against Gram-positive and Gram-negative bacteria and attributed this activity to the presence of the quaternary ammonium group in the organoclays. In contrast, they reported that Cloisite-Na⁺ shows no antibacterial activity, even though it has the same basic structure as the other 2 nanoclays. The use of different organic modifiers in the clays may contribute to the observed differences in AM activity.

Costa and others (2011) used Ag⁺-MMT NPs (in powder form) to enhance the stability of kiwi pineapple salad. The Ag⁺-MMT powder (10, 15, or 20 mg) was placed on the bottom of boxes containing 50 g cut fruit and 70 mL of 25% (w/v) fructose syrup. The growth of mesophilic and psychrotrophic bacteria and yeasts was reduced by the NPs. In other examples, Cruz-Romero and others (2013) demonstrated the AM activity of nanosized benzoic acid and sorbic acid against *E. coli* and Kim and others (2009) showed that TiO₂ coated onto glass reduced the growth of *E. coli*, *Listeria*, *S. aureus*, and *Salmonella* by 2.8 log CFU/mL.

Factors affecting applications of NPs

The potential application for a given type of NP depends on many factors, including material type (Ren and others 2009) as well as particle shape and concentration in the packaging matrix (Zhang and others 2007; Rhim and others 2009). The intrinsic properties of a NP are determined predominantly by its shape, size, composition, crystallinity, and morphology (Vigneshwaran and others 2006; Artiaga and others 2015). Numerous studies have suggested that species such as nanosilver, nanocopper, metal oxides such as TiO₂ and ZnO, as well as organically modified nanoclay such as quaternary ammonium modified MMT, are the most common materials that are used in the fabrication of nanocomposite materials for the purpose of providing an antibacterial property (Silva and others 2011). Previous studies have reported that such NPs possess both fungistatic and antibacterial activities against a wide range of microorganisms (Emamifar and others 2010b).

NPs in migrating and nonmigrating systems

Typically, AM packaging systems may be regarded as migrating or nonmigrating, with the distinction depending on the specific AM agent used and on its interactions with the packaging and the food matrix (Sanchez-Garcia and others 2010). In a migrating system, the NPs are released from the film into the package headspace and onto the food surface. Such systems are most useful when direct contact between the film and food product is not required for AM activity (Avella and others 2005; Sánchez-Valdes

and others 2009; Silva and others 2011; Silvestre and others 2011; de Azeredo 2013; Rhim and others 2013). The nonmigrating systems involve materials where the NPs and/or nanomaterials are immobilized within the material (Sadeghnejad and others 2014), and these systems can be applied where there is direct contact between the food and the packaging material (Makwana and others 2014).

The mode of action of NPs as an AM agent is influenced by their controlled and slow release onto the food surface (Pinto and others 2009). This is required in order to maintain an adequate concentration of the agent on the food and effectively inhibit microbial growth throughout the product shelf-life (Cooksey 2005; Tunç and Duman 2011). As stated by Han (2003), the mass transfer rate of an AM agent should not be faster than the growth rate of the target microorganism so that the agent is not depleted too quickly and adequate AM activity is maintained for a suitable time.

Test methods for determining efficacy of AM systems containing NPs

There are a number of test methods used to determine the AM activity in these systems and these include diffusion assays (agar diffusion) (Rhim and others 2006; Li and others 2010; Sadeghnejad and others 2014) and dilution methods (broth and agar dilution) (Pinto and others 2009; Li and others 2010). The agar diffusion method has been widely used in the past for molecular AM systems and can be applied to the study of systems containing NPs, but the results obtained from this technique are only qualitative. Although Table 3 contains a large amount of information on the activity of NPs successfully incorporated into various polymeric materials, comparison between the different systems is often difficult because of the wide variations in the experimental conditions utilized in the various studies.

Specific NP applications in AM systems

In general, an AM packaging system can be produced by: (i) directly incorporating NPs into a conventional packaging film (Li and others 2009b; Xing and others 2012; Panea and others 2014) or (ii) coating the packaging film with NPs (Tankhiwale and Bajpai 2012; Othman and others 2014; Sadeghnejad and others 2014) and their release controlled to regulate their activity (Ruparella and others 2008). Table 3 summarizes the various food packaging formulations containing NPs that are either incorporated into or coated onto a polymeric substrate.

Systems based on natural polymers. Polysaccharide-based polymers can be used for the production of biodegradable films that have the potential to be used in AM food packaging systems when incorporated with NPs (Arora and Padua 2010; Espitia and others 2013). As shown in Table 3, significant progress has been made by effectively integrating NPs into various polysaccharides such as starch-based films, and many of these demonstrate inhibitory activity against the growth of various microorganisms including *S. enteritidis*, *L. plantarum*, *B. thermosphaceta* B2, *L. monocytogenes*, *E. coli* O157:H7, *E. coli*, *S. aureus*, and *S. typhimurium*. For example, Heydari and others (2013) incorporated a range of Na⁺-MMT NPs with concentrations from 0–5% (w/w) into corn starch film and investigated the AM activity of the NPs on the growth of *E. coli* and *S. aureus* using the agar diffusion method. They reported that the additive effectively inhibits the growth of these microorganisms. Tankhiwale and Bajpai (2012) reported AM activity against *E. coli* using 2% (w/w) ZnO NPs in starch coated onto polyethylene. Nafchi and others (2012) also studied the AM

Table 3—Examples of nanoparticles for potential use in antimicrobial food packaging systems.

Packaging	Nanomaterial	Loading	Organisms	Observations	Reference
—	Ag ⁺ -MMT	10 mg 15 mg 20 mg	Mesophilic and psychrotrophic bacteria and yeasts	Bacteria and yeasts reduced	Costa and others (2011)
—	Cloisite 30B Cloisite 20A Cloisite Na ⁺	5% (w/w)	<i>S. aureus</i> , <i>L. monocytogenes</i> , <i>S. typhimurium</i> , <i>E. coli</i> O157:H7	Cloisite 30B NPs showed highest antibacterial activity Exhibits AM activity against tested organisms Did not demonstrate AM activity against all microorganisms tested	Hong and Rhim (2008)
PLA	Cloisite 30B	5% (w/w)	<i>L. monocytogenes</i> , <i>S. aureus</i> , <i>E. coli</i> O157:H7, <i>S. typhimurium</i>	Film effective against <i>L. mono-cytogenes</i>	Rhim and others (2009)
PLA	C93A C30B	3% (w/w)	<i>E. coli</i> , <i>L. monocytogenes</i> , <i>S. typhimurium</i>	Reduced growth of all species Inhibited all species	Darie and others (2014)
PLA	Ag-nanoclay	1% (w/w)	<i>Salmonella</i> spp.	Reduced 2.44 × 10 ⁷ to 5.24 × 10 ⁴ CFU/mL	Busolo and others (2010)
PLA	ZnO	—	<i>Salmonella enterica</i>	Reduced 3 to 4 log CFU/mL on liquid egg	Jin and Gurtler (2011)
PLA	ZnO	1% to 3% (w/w)	<i>S. aureus</i> , <i>E. coli</i>	Significant AM activity observed against both species	Pantani and others (2013)
PLA	Na ⁺ -MMT	0% to 5% (w/w)	<i>S. aureus</i> , <i>E. coli</i>	AM activity against both species	Heydari and others (2013)
Starch coatings	ZnO	2% (w/v)	<i>E. coli</i>	Inhibition observed	Tankhwal and Bajpai (2012)
Starch	ZnO nanorods	—	<i>S. aureus</i> , <i>E. coli</i>	Antibacterial activity against both species	Nafchi and others (2012)
Chitosan	MMT	—	<i>S. aureus</i> , <i>E. coli</i>	Reduced growth <i>in vitro</i>	Han and others (2010)
Chitosan	Cu	20% (v/v)	<i>S. aureus</i> , <i>S. typhimurium</i>	Reduction of 3 to 4 log CFU/mL	Cardenas and others (2009)
Chitosan	Ag	—	<i>B. cereus</i> , <i>S. aureus</i> , <i>E. coli</i>	Reduced growth of all species	Yoksan and Chirachanchai (2010)
Chitosan	Ag	—	<i>E. coli</i>	Reduced growth	Sarpui and others (2008)
Chitosan	Ag	—	<i>S. aureus</i> , <i>S. typhimurium</i> , <i>E. coli</i> , <i>L. monocytogenes</i>	Only effective against <i>S. aureus</i> and <i>L. monocytogenes</i>	Rhim and others (2006)
Agar films	Cloisite 30B Ag ⁺ -MMT	—	—	Significantly increased shelf-life of cheese without affecting its functional dairy microbiota	Incoronato and others (2011)
Agar	ZnO	3 mg/L	<i>S. typhimurium</i> , <i>S. aureus</i>	Population of both species reduced by ca. 2 log within 24 h	Akbar and Anal (2014)
Calcium alginate coatings	Ag ⁺ -MMT	—	—	Prolonged shelf-life of carrots for ca. 70 d <i>cf.</i> 4 d for uncoated samples	Costa and others (2012)
Hydroxy-apatite	Cu or ZnO	—	<i>E. coli</i> , <i>S. aureus</i> , <i>C. albicans</i>	Reduced viable cells counts for all species in liquid culture	Stanic and others (2010)
Cellulose	Cu	—	<i>E. coli</i>	Inhibitory activity observed	Mary and others (2009)
Cellulose	Ag	—	<i>K. pneumoniae</i>	Growth suppression by >5.0 log CFU/mL on potato dextrose agar	Pinto and others (2009)
Cellulose	Ag	—	<i>E. coli</i> , <i>S. aureus</i> , <i>Mesophilic</i> bacteria	Films reduced the population of all species by 1 to 3 log CFU/mL	Fernandez and others (2010)

(Continued)

Table 3–Continued

Packaging	Nanomaterial	Loading	Organisms	Observations	Reference
HPMC	Ag		<i>E. coli</i> , <i>S. aureus</i>	Bactericidal effects against both species	De Moura and others (2012)
MC	ZnO	17% (w/w)	<i>S. aureus</i> , <i>L. monocytogenes</i>	AM activity exhibited against both species	Espitia and others (2013)
WPI	Cloisite 20A, Cloisite Na ⁺	5% (w/w)	<i>E. coli</i> O157:H7, <i>L. monocytogenes</i>	No AM activity	Sothornvit and others (2009)
FPI	Cloisite 30B	3% (w/w)	<i>L. monocytogenes</i> , <i>P. aeruginosa</i>	Significant AM activity against <i>L. monocytogenes</i> .	Arfat and others (2014)
Gelatin-based films	ZnO	3% (w/w)	<i>E. coli</i> , <i>L. monocytogenes</i>	Inhibited growth of both species	Kanmani and Rhim (2014b)
LDPE	Ag	10% (w/w)	<i>P. aeruginosa</i> , <i>L. monocytogenes</i> , <i>E. coli</i>	AM activity against both species	Panea and others (2014)
LDPE	Ag, ZnO	10% (w/w)	<i>P. aeruginosa</i> , <i>L. monocytogenes</i> , <i>E. coli</i>	AM activity both <i>in vitro</i> and on meat	Panea and others (2014)
LDPE	TiO ₂	3% (w/w)	<i>Pseudomonas</i> spp., <i>Rhodotorula mucilaginosa</i>	<i>Pseudomonas</i> spp. reduced by 4 log CFU/mL, <i>R. mucilaginosa</i> decreased by 2 log CFU/mL	Bodaghi and others (2013)
LDPE	Ag	0.6% and 1% (w/w)	<i>Pseudomonas oleovorans</i> on agar, <i>A. niger</i>	Inhibitory effects against both species	Sánchez-Valdes and others (2009)
LDPE	Ag	1.5% to 5% (w/w)	Yeast, moulds, total aerobic bacteria	Suppressed growth of all species in orange juice	Emamifar and others (2010a,b)
LDPE	ZnO	0.25% to 1% (w/w)		Reduced growth of yeasts and molds	Bruna and others (2012)
LDPE	Cu ²⁺ -MMT	4%	<i>E. coli</i> O157:H7	Population reduced by 94%	Sadeghnejad and others (2014)
LDPE	Ag		<i>E. coli</i> , <i>S. aureus</i>	Inhibited growth of both species	Sadeghnejad and others (2014)
PE	TiO ₂	2% (w/w)	<i>E. coli</i> , <i>S. aureus</i>	Films exhibited antibacterial activity against both species	Xing and others (2012)
PVC	ZnO	10% (w/w)	<i>E. coli</i> , <i>S. aureus</i>	Film exhibited inhibitory effect on both species	Li and others (2010)
PVP	Ag		Psychrotrophic bacteria	Increase in shelf-life of asparagus and pears by 10 d	An and others (2008)
EVOH	TiO ₂		<i>Bacillus</i> spp., <i>E. coli</i> , <i>L. plantarum</i> ,	Increased AM activity against tested bacteria	Cerrada and others (2008)
Glass	TiO ₂		<i>E. coli</i> , <i>Listeria</i> , <i>S. aureus</i> , <i>Salmonella</i>	Reduction of up to 2.8 log CFU/mL	Kim and others (2009)
Oriented PP	TiO ₂		<i>E. coli</i>	Reduction of 1 log CFU/mL on lettuce	Chawngkijwanich and Hayata (2008)
PVC	ZnO		<i>E. coli</i> , <i>S. aureus</i> , psychrotrophic bacteria	Inhibition zones and low decay	Li and others (2009b)
Polyamide-6 films	Ag	1.9% (w/w)	<i>E. coli</i>	Reduced growth of from 1.8 × 10 ⁶ to 3.8 × 10 ⁵ CFU/mL	Damm and others (2008)

activity of ZnO nanorods impregnated into sago starch films and demonstrated antibacterial activity against *S. aureus* and *E. coli*.

Incoronato and others (2011) incorporated Ag⁺-MMT NPs into agar films with the aim of preserving cheese. The authors claimed that the Ag⁺-MMT particles markedly increased the shelf-life of the cheese without affecting its functional dairy microbiota and sensory quality compared to the control film. In an earlier study, the same research group reported that an agar matrix incorporated with Ag⁺-MMT NPs exhibited AM activity compared with zein and poly(caprolactone) nanocomposites (Incoronato and others 2010). Moreover, Costa and others (2012) incorporated Ag⁺-MMT NPs into calcium alginate coatings on oriented PP bags. They reported that the coatings prolonged the shelf-life of carrots for about 70 d compared with 4 d for the uncoated samples. More recently, Akbar and Anal (2014) incorporated ZnO NPs into alginate films and investigated the AM activity of these systems against *S. aureus* and *Salmonella typhimurium* on the surfaces of ready-to-eat poultry meats. They claimed that the NPs were highly effective against both of these species.

The AM activity of biopolymer films such as chitosan has been widely investigated and, in general, chitosan films impregnated with NPs exhibit inhibitory activity towards the growth of various microorganisms. For example, Han and others (2010) developed chitosan/MMT nanocomposites and found that these materials successfully reduced the growth of *S. aureus* and *E. coli* during *in vitro* experiments. Cardenas and others (2009) also reported AM activity against *S. aureus*, and *S. typhimurium* by incorporating nanocopper into chitosan films, with a 3 to 4 log CFU/mL reduction of these species. Yoksan and Chirachanchai (2010) showed that chitosan-starch films impregnated with silver NPs reduced the growth of *B. cereus*, *S. aureus*, and *E. coli* on agar media after 24 h at 37 °C. Sanpui and others (2008) studied the antibacterial effectiveness of nanosilver impregnated into chitosan films against *E. coli* and the composite films were reported to be effective against the bacteria. Rhim and others (2006) developed chitosan films containing 5% (w/w) Cloisite 30B or nanosilver and studied the antibacterial activity against *S. aureus* and *S. typhimurium*, *L. monocytogenes*, and *E. coli* O157:H7 by the inhibition zone method. It was reported that the Cloisite 30B nanocomposite film exhibited AM activity against 2 Gram-positive bacteria (*S. aureus* and *L. monocytogenes*) but not against 2 Gram-negative species (*S. typhimurium* and *E. coli* O157:H7). Conversely, the authors reported that nanosilver/chitosan films exhibited clear inhibition zones against all of the 4 test microorganisms and this suggests that nanosilver provides a broad spectrum of AM activity.

Several researchers have investigated the AM activity of NPs incorporated into PLA-based films. Busolo and others (2010) incorporated 1% (w/w) silver-nanoclay into PLA film and reported a 99.8% reduction in the population of *Salmonella* spp compared with the control film. Jin and Gurtler (2011) reported that PLA-ZnO coated onto a glass jar reduced the growth of *Salmonella enteric* against liquid egg. Pantani and others (2013) developed an AM film based on PLA incorporated with ZnO at different concentrations and reported a significant reduction of *E. coli* and *S. aureus* in liquid culture. Darie and others (2014) developed PLA nanocomposite films containing the nanoclays Cloisite 93A and Cloisite 30B and found that these nanoclays successfully reduced the growth of *E. coli*, *P. aeruginosa*, and *S. aureus* during *in vitro* experiments.

Other studies have evaluated the AM activity of NPs incorporated into cellulose-based materials such as methylcellulose (MC) films and/or their derivatives such as hydroxypropylmethylcellu-

lose (HPMC). The cellulose-based materials are naturally occurring polysaccharides with adequate film-forming properties (Espitia and others 2013), but there have been only a limited number of studies conducted using MC-based materials for AM applications. More recently, there has been an increased recognition of the potential use of cellulose-based materials in AM packaging systems (Lagarón and Fendler 2009). For example, Mary and others (2009) incorporated nanocopper into cellulose film and observed AM activity of the nanocomposite against *E. coli* on solid media. Fernandez and others (2010) examined the inhibitory effects of nanosilver incorporated into cellulose film against the growth of *E. coli* and *S. aureus* using the agar diffusion assay and found there was significant inhibitory activity. Similarly, Pinto and others (2009) incorporated nanosilver into cellulose film and evaluated the antimycotic activity of this agent on the growth of *K. pneumoniae* using a liquid culture. They claimed that the nanosilver suppressed the growth of the microorganism by >5.0 log CFU/mL on potato dextrose agar. The AM activity of HMPMC incorporated with silver NPs against *E. coli* and *S. aureus* has also been reported by De Moura and others (2012). Moreover, Espitia and others (2013) demonstrated the antibacterial effectiveness of ZnO NPs incorporated into MC films against *S. aureus* and *L. monocytogenes* in an agar disc diffusion test.

The AM activity of various NPs incorporated into protein-based films has been reported by a number of different researchers. Recently, Kanmani and Rhim (2014a) examined the AM activity of nanosilver incorporated into gelatin-based films against *E. coli* and *L. monocytogenes* on laboratory media. It was found that the films demonstrated inhibition against both of these foodborne pathogens. Arfat and others (2014) developed a fish protein isolate (FPI) film containing 3% (w/w) ZnO NPs and evaluated the AM efficacy of these active nanocomposite films against *L. monocytogenes* and *P. aeruginosa* in a disc diffusion assay. They reported that the FPI films inhibited the growth of these species. Sothornvit and others (2009) reported that a WPI composite of Cloisite 20A exhibited little AM activity, however Cloisite 30B in the film was active which may be due to the different organic modifier used in that nanoclay.

Systems based on synthetic polymers. Nanocomposite materials have been developed for AP applications based on the incorporation and/or coating of NPs into/onto synthetic polymers. Packaging films made from the more traditional synthetic polymers such as LDPE, ethylene vinyl alcohol (EVOH), PP, and PVC possess adequate and reliable physicomechanical properties (An and others 2008; Li and others 2009b; Emamifar and others 2010b; Sadeghnejad and others 2014). NPs including nanosilver, ZnO, and TiO₂ have been successfully incorporated into LDPE films with a number of studies claiming these materials exhibit AM activity. A summary of the studies investigating the antibacterial effect of NPs in synthetic petroleum-based polymer films is also presented in Table 3. For example, Emamifar and others (2010b) incorporated nanosilver and ZnO into LDPE film and investigated the AM activity of the NPs on the growth of total aerobic bacteria, yeasts, and molds on and in orange juice. They reported that 1.5% and 5% (w/w) of nanosilver suppressed the growth of all of these microorganisms, whereas film formulations containing 0.25% (w/w) or 1% (w/w) ZnO reduced the growth of yeasts and molds. The latter film inhibited the growth of aerobic bacteria on and in orange juices and extended the shelf-life of the orange juice to 28 d. Sadeghnejad and others (2014) incorporated nanosilver into LDPE films to control the growth of *E. coli* and *S. aureus* and assessed the effectiveness of the formulations using

the agar diffusion method. It was found that the nanosilver in these films inhibited the microbial growth of both microorganisms after 1 d of storage at 37 °C.

Sánchez-Valdes and others (2009) developed active LDPE films incorporated with nanosilver and claimed an inhibitory effect against the growth of *Pseudomonas oleovorans* on agar and *A. niger* on potato dextrose agar. Wang and others (2005) investigated the antibacterial activity of LDPE films containing TiO₂ NPs prepared as a master batch by melt-blending. In their studies, Bruna and others (2012) incorporated nanocopper-modified MMT (MMT-Cu²⁺) into LDPE films and reported an antibacterial effect against *E. coli* O157:H7 in laboratory media. They claimed that 4% (w/w) of the additive in the film reduced 94% of bacterial colonies. In another example, Li and others (2009a) reported that a PE film incorporated with nanosilver reduced the aging of jujube, a Chinese fruit. Xing and others (2012) examined the AM activity of 2% (w/w) TiO₂ NPs incorporated into a PE-based film against the growth of *E. coli* and *S. aureus* inoculated on laboratory media and observed an inhibitory effect against both of these microorganisms.

Nanocomposite materials have also been developed for AP systems based on the incorporation of NPs into PVC, poly(vinylpyrrolidone) (PVP), PA, EVOH, and PP films. Li and others (2009b) reported inhibition zones against the growth of *E. coli*, *S. aureus*, and psychrotrophic bacteria by ZnO incorporated into PVC. In another study, Li and others (2010) introduced 10% (w/w) ZnO into PVC film and investigated the AM activity of the film against *E. coli* and *S. aureus*. An inhibitory effect against each of the microorganisms was reported. An and others (2008) coated nanosilver onto PVP to control the growth of psychrotrophic microorganisms on asparagus and pears. It was found that the formulations were effective in decreasing microbial growth and extending the shelf-life of asparagus by 10 d. Damm and others (2008) incorporated nanosilver into PA-6 films and claimed that 1.9% (w/w) of nanosilver incorporated into these films reduced the growth of *E. coli* by 79% after 24 h at room temperature.

In a recent study, Ni and others (2014) demonstrated that nanosilver inhibited the growth of *E. coli*, *S. aureus*, and *P. aeruginosa* on culture media. They claimed that nanosilver incorporated into modified poly(acrylic acid) exhibits excellent antibacterial properties. Cerrada and others (2008) introduced 1% (w/w) TiO₂ NPs into EVOH film by compounding the particles with EVOH wax prior to extrusion with EVOH *via* a single-screw extruder and film-blowing. These films successfully reduced the growth of *Bacillus spp.*, *E. coli*, and *L. plantarum*. Chawengkijwanich and Hayata (2008) investigated the AM activity of TiO₂ incorporated into oriented PP against *E. coli* on solid and in liquid media and showed effective inhibition of the bacterium by reducing its growth by 1.0 log CFU/mL. The findings of these studies suggest that packaging materials containing TiO₂ NPs as AM agents demonstrate potential for application in AM food packaging applications.

Consumer concerns

Notwithstanding the potential benefits of the application of NPs in food packaging technology, the downside to this technology is the possible risk of these particles migrating from the packaging material into the foodstuff, which could then pose a risk to human health (Faunce and Watal 2010; de Azeredo 2013; Echegoyen and Nerín 2013; Fortunati and others 2013; Rhim and others 2013; Panea and others 2014). Incorporated NPs can migrate from the packaging material into the food *via* diffusion, or slow

release, ultimately leading to ingestion of NPs by consumers. Such migration of NPs might also cause adverse organoleptic changes to foodstuffs (de Azeredo 2013; Dhawan and others 2014; Panea and others 2014). The main concerns stem from the lack of knowledge about the potential effects and impacts of nanosized materials on human health (Chaudhry and Castle 2011), but this is now starting to be addressed by researchers (Cheng and others 2013; Esch and others 2014).

In general, the chemical and biological properties of nanomaterials can be substantially different from those in their conventional forms, and therefore their effects and impacts may not be accurately predicted from the existing knowledge on micro and/or macro forms (Chaudhry and Castle 2011). However, data pertaining to the migration of NPs from packaging into foodstuffs is limited, thus posing a significant barrier to the assessment of the main risks of consumer exposure to NPs in food packaging (Bradley and others 2011). Several researchers have suggested that the potential migration of NPs from packaging to foodstuffs has not been fully investigated nor has it been appropriately characterized in many cases (Lorenz and others 2012; Xu and others 2012; de Azeredo 2013; Nowack and others 2013; Rhim and others 2013). To address the problem of possible migration of NPs, there has recently been much research effort devoted to the development of analytical protocols to better characterize the detection of NPs and determine their potential for migration into foods. These have been discussed in a previous section of this review.

In addition to the potential safety concerns associated with food packaging materials containing engineered NPs, the design of modern AP packaging systems must also take into account the inherent toxicity that has been associated with several types of petroleum-derived polymers. For example, the processing of PVC requires the use of plasticizers such as phthalates to render the material malleable and easily processable but these additives have the potential to migrate from the polymer and enter the food chain (Erythropel and others 2014). Phthalates are particularly concerning because of their link with endocrine disruption so some alternatives to these plasticizers have been developed including plant based derivatives obtained from soybean oil (Bueno-Ferrer and others 2010), sunflower oil (Rouane and others 2014), and palm oil (Ang and others 2014). The migration of phthalates from PET has also been widely reported (Bošnjir and others 2007; Schmid and others 2008; Pinto and Reali 2009; Bach and others 2012) as well as the migration of styrene from PS (Murphy and others 1992; Date and others 2002; Choi and others 2005; Khaksar and Ghazi-Khansari 2009).

It is clear from the studies reported in Table 1 to 3 that the use of nanomaterials for physico-mechanical property improvement of petroleum-based polymers is relatively limited compared to their use in biopolymers for food packaging. The increased popularity and growth in biopolymer materials for packaging may be a combination of consumer concerns with some conventional polymeric materials as well as environmental and sustainability concerns. Unfortunately, it is also evident that many biopolymers are not suitable replacements for conventional packaging applications without modification to improve performance or impart a specific functional activity. The use of engineered NPs offers a pathway to modification but the potential for particle migration, just as the potential for chemical migration from some types of conventional packaging materials, must be clearly addressed to satisfy both consumers and regulators alike.

Conclusions

In recent years, more and more applications of nanotechnology have emerged in the food industry, and future developments hold great potential for AP systems intended to protect food products from microbial contamination. Many NPs incorporated into or coated onto polymer-based packaging materials have demonstrated significant AM activity against various microorganisms. The incorporation of certain nanomaterials into polymers has been reported to improve physicomechanical properties, which is also of great interest for applications in food packaging. Although many polymeric materials incorporated with various nanomaterials have demonstrated the potential use in AM food packaging, an important aspect to be considered is the potential for migration of these particles into food products. Furthermore, at present, there is a challenge associated with the detection, characterization, and quantification of NPs in food because of the variation and complexity associated with food compositions. Moreover, a distinction must be made between migrated particles and ionic species within the limitations of currently available experimental techniques. In general, the results of reported migration studies to date reveal that only relatively low levels of particles or ions migrate into various food simulants. Although this is encouraging, the current knowledge on the migration of nanomaterials and their effects is limited and further work is necessary to fully assess any associated risks to human health and the environment. Thus, future research will be needed to develop strategies to detect, quantify, and categorize NPs in complex food matrices and to enhance the experimental techniques for the characterization of NPs so that these additives can be safely used in AM food packaging systems.

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Author Contributions

Kuorwel K. Kuorwel searched and reviewed the relevant literature and drafted the manuscript; Marlene J. Cran, John D. Orbell, Saman Buddhadasa, and Stephen W. Bigger equally edited the original manuscript and provided input on the design of this review and its table structures; Marlene J. Cran and Stephen W. Bigger performed the major final revision.

Nomenclature

AAS	atomic absorption spectroscopy
AES	atomic emission spectroscopy
AFFFF	asymmetrical flow field flow fractionation
AP	active packaging
AM	antimicrobial
CFU	colony-forming units
CMC	carboxymethylcellulose
DLS	dynamic light scattering
EVA	ethylene vinyl acetate copolymer
EB	elongation at break
EVOH	ethylene vinyl alcohol
FFF	field flow fractionation
FPI	fish protein isolate
GC	Gelidium corneum
GCG	Gelidium corneum gelatin
HDPE	high-density polyethylene
HPMC	hydroxypropylmethylcellulose

ICP	inductively coupled plasma spectroscopy
LDH	layered double hydroxide (anionic clays)
LDPE	low-density polyethylene
LLDPE	linear low-density polyethylene
MALS	multi-angle light scattering detection
MC	methylcellulose
MCC	microcrystalline cellulose
MMT	montmorillonite
MS	mass spectrometry
NP	nanoparticle
OES	optical emission spectroscopy
PA	polyamide
PE	polyethylene
PET	poly(ethylene terephthalate)
PHA	poly(hydroxyalkanoate)
PLA	poly(lactic acid)
PP	polypropylene
PS	polystyrene
PVC	poly(vinyl chloride)
PVP	poly(vinyl pyrrolidone)
RH	relative humidity
RT	room temperature
SP	soy protein
SPI	soy protein isolate
TPS	thermoplastic starch
TS	tensile strength
WPI	whey protein isolate
WVP	water vapor permeability
YM	Young's modulus

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