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Recent advances in polymer-metallic composites for food packaging applications

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ABSTRACT

Background: The use of metallic micro- and/or nanoparticles as inorganic fillers for the improvement of polymer properties is an active trend. This has led to the development of polymer-metallic composites with high potential to be applied in food packaging, due to the enhanced antimicrobial, gas barrier, light-blocking and antioxidant effect in addition to the polymer intrinsic properties. The increasing number of investigations of novel polymer-metallic composites with promising potential and/or already applied as food packaging has raised concern over their efficacy, but also toxicity and environmental impact.

Scope and approach: In this review a critical evaluation of current investigations on polymer-metallic composites, as food packaging options, is assessed. This evaluation emphasizes the enhanced properties provided by the metallic fillers onto the polymer packaging itself, and indirectly in food shelf life, safety and quality. Moreover, awareness regarding the toxicity and environmental impact is also evaluated and related to the migration behaviour.

Key findings and conclusions: Without question, the addition of these type of fillers has the enormous potential to enhance the package properties and, therefore, the food shelf life. Usually, their addition is made alone or in complementation with other fillers allowing a broad spectrum of enhanced properties in the composite film. Despite the advantages, special attention must be paid to the migration form of the filler, in the ionic or the particulate form, that is related to the toxicity and environmental impact of such materials. In overall, the strengths and weaknesses are critically organized, allowing guidance decisions on the implementation of such materials in food packaging.

1. Introduction

Food packaging, in addition to its usual job of containing the food product, it is also responsible for ensuring the freshness, taste and nutritional value of the product, thus leading to a prolonged shelf life and safer food supply. According to AMERIPEN (American Institute for Packaging and Environment) around 20–25% of food waste can be avoided by the application of food packaging technologies, and consequently, decrease the environmental impact associated to the food waste (AMERIPEN, 2020). As a result, achieving a reduction in the food loss or waste by using novel food packaging technologies, that improve the food shelf life, safety and quality, has gained an increased interest among the academic and industry sectors.

Active food packaging is amongst these novel technologies (Realini & Marcos, 2014). This consists in the incorporation of fillers into the food package, which in turn can interact with the food and/or the package headspace, for example, by the removal (scavenging) of gas molecules (*e.g.,* oxygen, water vapour or carbon dioxide) or the release of antimicrobial agents (capable of controlling and inhibit the microbial growth), and thus protecting the food product (Duncan, 2011). Intelligent food packaging is another technology used, being related to the capability of monitoring the status of the food product inside the package and its surroundings by using sensors or indicators (Realini & Marcos, 2014).

Application of inorganic micro- and/or nanomaterials has become one of the main pathways to achieve active and intelligent packaging.

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These can be applied in sachets, absorbent pads, sensors, or incorporated into the food contact package as fillers inside the polymer matrix or as coatings in the polymer surface, producing the so-called polymer micro- and nanocomposites (Ariyarathna, Rajakaruna, & Karunaratne, 2017; Ogunsona, Muthuraj, Ojogbo, Valerio, & Mekonnen, 2020; Realini & Marcos, 2014). Various inorganic fillers such as, carbon-based materials (*e.g.*, carbon nanotubes, graphene, etc.), clays, metal oxides (*e.g.*, ZnO, MgO, TiO_2, CuO, Al_2O_3, CaO, SiO_2, etc.), and zero valent metallic micro-/nanoparticles (*e.g.*, Fe, Ag, Cu, Au, Pd, Pt, Cd, Zn, Se, etc.), that from this point on will be referred as M_0F (*i.e.*, metallic fillers), are largely employed to produce polymer composites to be applied in food packaging (Ariyarathna et al., 2017; Duncan, 2011; Realini & Marcos, 2014).

With the increasing demand for packed food products with extended shelf life, much attention has been made over the years into the fabrication of polymer-metallic composites (PM_0C) by the incorporation of M_0F. This is due to their unique physicochemical properties that guarantee active effects, such as antimicrobial (*e.g.*, Ag and Cu), scavenging of gas molecules (*e.g.*, Fe or Pd), antioxidant, (*e.g.*, Se), but also, enhanced polymer intrinsic properties (*e.g.*, thermal, mechanical, optical, rheological properties etc.), leading to PM_0C with great future as active food packaging options (He, Deng, & Hwang, 2019; Santos, Ingle, & Rai, 2020).

In intelligent packaging, M_0F can also be used to develop technologies in order to monitor food quality and safety. For example, a real-time monitor device for meat spoilage was developed using a colorimetric hydrogen sulphide (H_2S) sensor based on AgNPs as indicator (Zhai et al., 2019). This sensor was centred on the ability of AgNPs to highly react to H_2S (that is considered a volatile gas produced during meat spoilage due to degradation processes of sulphur-based amino acids) to form silver sulphide (Ag_2S), that causes the colour fading of the yellow AgNPs to a blank colour.

Given the enormous progress made in nanotechnology, its spread into the fabrication of nano-based food packaging technologies was inevitable, and currently, several reviews regarding the application of nanotechnology in food packaging are available. However, their focus is somewhat general, involving a great variety of nanomaterials (Ariyarathna et al., 2017; Hoseinnejad, Jafari, & Katouzian, 2018; Ogunsona et al., 2020), or focused on particular fillers such as metal oxides (Garcia, Shin, & Kim, 2018), and few are fully centred in the use of zero valent M_0F as fillers in food packaging (Santos et al., 2020). Therefore, the aim of this review is to evaluate the current advances of polymer composite films with incorporated M_0F with promising potential and/or already applied as food packaging. In this review, literature that performed indirect tests (*i.e.*, with "promising potential"; *e.g.*, antibacterial, gas barrier, etc.) and direct food model testing (*i.e.*, "already applied") to prove the PM_0C effectiveness as food packaging, was included.

The main objectives of this review are to give the readers: (i) a critical overview of the latest PM_0C technologies, (ii) the strengths and weaknesses of such systems, and (iii) the current challenges regarding their implementation in the market. Furthermore, in this work, the PM_0C are classified based on the type of inorganic fillers introduced into the polymer matrix. To achieve these goals, a summary on the advantages of PM_0C as food packaging is discussed, in terms of antimicrobial action, antioxidant abilities, gas barrier effects, UV–vis protection, polymer intrinsic properties (thermal, mechanical, optical, etc.) and others. Additionally, several concerns and problems regarding the application of PM_0C in food packaging are discussed, with a focus on the regulations, migration, toxicity and the environmental impact. Recent literature is reviewed to present the readers the current state of the art about the use of PM_0C with potential to be applied as food packaging materials.

2. Food packaging related properties given by M_0F

It is necessary to acknowledge the mechanisms behind the antimicrobial and gas barrier properties by which sole M_0F act, in order to understand the same active effects on PM_0C. The effectiveness of M_0F against a wide spectrum of microorganisms (bacteria, fungi, viruses and yeasts) has been widely reported. However the mechanisms behind their activity are varied and not fully elucidated yet (Ogunsona et al., 2020). It is of general thinking that a two-side effect occurs, being resulted from a simultaneous or asynchronous action of the direct contact of the inorganic metallic particle with the microorganism and the action of the liberated metallic ionic form.

This two-sided action causes, more specifically, antimicrobial effects that can be resumed and associated with (i) the release of the metal ions that can disrupt the ATP production and DNA replication; (ii) binding with cell membrane biomolecules leading to its disruption; (iii) physical damage by the direct contact of the particle with the microorganism, often observed by the formation of pits in the bacteria cell membrane, causing damage and/or possible penetration into the cell depending on the particle size; and (iv) the generation of reactive oxygen species to damage the DNA (Ogunsona et al., 2020; Tamayo, Azócar, Kogan, Riveros, & Páez, 2016).

Regarding on how M_0F inside the polymer matrix can provide antimicrobial action, there is a consensus opinion that the mechanism is based on a releasing system, in which the metallic ions (due to oxidation of the metallic filler) are the main responsible for the antimicrobial activity. This is also believed to be present in all PM_0C (Fig. 1A and C) (Ogunsona et al., 2020). However, the direct release of the M_0F in the inorganic particulate form from the polymeric matrix is also a possibility, and thus, the antimicrobial activity of migrated metallic particles in complementation with the action of the metallic ions cannot be ruled out (Fig. 1B and D). As a result, there is a strict connection of the antimicrobial activity with the migration capability of the incorporated M_0F. In the end, the released ions and/or particles will provide the antimicrobial action by the distinct pathways previously described.

Improving the barrier of food packages against oxygen, water vapour and/or carbon dioxide (Fig. 1E), is incredibly important in food products in order to maintain product shelf life, quality and safety. Enhanced

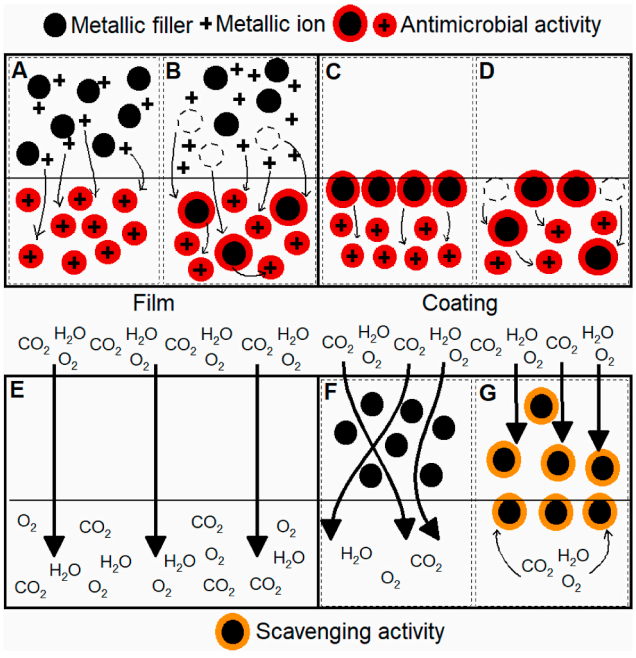

Fig. 1. Scheme regarding the possible antimicrobial mechanisms of polymer-metallic composites by metallic ion release (A and C) due to metallic particle oxidation and/or simultaneous metallic ion and full particle release (B and D). Moreover, schemes regarding the barrier mechanisms of polymer-metallic composites are illustrated in E, F and G. Arrows indicate the direction of the release and the empty circles represent the absence of particle.

barrier properties of PM_0C can be related to (a) the tortuous path effect provided by the incorporated inorganic fillers, as passive property, that leads to an increased path length regarding gas diffusion (*i.e.*, the travelling of gas molecules) and thus decreasing the permeability (Fig. 1F) (Duncan, 2011); and to (b) the presence of a scavenging system (active property) able to remove the gas molecules present in the headspace and/or impede their permeability from the exterior of the package (Fig. 1G). This last mechanism depends on the type of M_0F, in which iron and palladium-based fillers are commonly applied. These will be briefly discussed in Section 3 (Gaikwad, Singh, & Lee, 2018). Moreover, induced changes in polymer intrinsic properties such as in the degree of crystallinity or reduced water uptake (hydrophobicity), will also influence the barrier properties of the PM_0C, with a higher degree of crystallinity and low water uptake being related to reduced gas permeability (Duncan, 2011).

As other functionalities in relation to food packaging, antioxidant and UV–vis barrier protection are also highlighted throughout the Section 3 as food packaging-related effects, induced by the incorporation of M_0F. The enhancement of the polymer intrinsic properties, in terms of thermal stability, mechanical properties (tensile strength, elastic modulus, elongation at break, etc.), and others, are also typical effects provided by the incorporated M_0F, allowing for more resistant food packaging films.

3. Classification of polymer-metallic composites

Based on the type of inorganic fillers that are introduced in the polymer matrix, in this work, the PM_0C are classified as binary, ternary and quaternary, as represented in Fig. 2. Binary-PM_0C (Fig. 2A), consist of a M_0F and a polymer side, and are represented as M_0F-polymer (*e.g.*, CuNPs-polymer). Ternary-PM_0C are characterized by having the M_0F added separately (M_0F1+F2-polymer, where M_0F1 is the metallic filler 1 and F2 is the filler 2*; e.g.*, AgNPs+SiO_2-polymer; see Fig. 2B) or physically/chemically immobilized within a second filler (M_0F1/F2-polymer; *e.g.*, AgNPs/SiO_2-polymer; see Fig. 2C), into the polymer matrix. These are generally called doped structures, in which a second filler that can be organic or inorganic is doped/decorated with a M_0F. These are here named as dual-side fillers (*e.g.*, AgNPs/SiO_2). In the case of quaternary-PM_0C, the M_0F is separately combined with two or more fillers (M_0F1+F2+F3-polymer, where F3 is the filler 3; *e.g.*, AgNPs+SiO_2+TiO_2-polymer; see Fig. 2D), or physically/chemically immobilized, named triple-side fillers (M_0F1/F2/F3-polymer; *e.g.*, AgNPs/SiO_2/TiO_2-polymer; see Fig. 2E), that are then added into the polymer matrix.

3.1. Binary polymer-metallic composites

Polymer-silver binary composites. Silver is, without question, the most used M_0F for the fabrication of PM_0C. The potent broad-spectrum antimicrobial capability of silver makes it useful to be applied in the food packaging field, with also improvements in the gas barrier, UV–vis barrier, and polymer intrinsic properties, as presented in Table 1.

Melt blending of M_0F into the polymer melt is the most applied mixing strategy when using thermoplastic polymers. However, one of the main problems is the agglomeration phenomena, that often leads to defects in the polymer properties, especially when using non-polar polymers (*e.g.*, LDPE or PP) which are immiscible and of non-interacting nature with most fillers. Thus, ensuring a proper homogeneous distribution in order to fully engage the properties of the M_0F is desired. For this, several techniques may be applied such as surface modification of the M_0F with functional groups, allowing a better interaction with the polymer matrix. Guozhou Cao et al. (Table 1) (Cao et al., 2018), synthesized surface modified AgNPs with dodecyl mercaptan to prepare AgNPs-PP binary films by melt blending. Despite the non-polar character of the PP, the surface modified AgNPs allowed a homogeneous dispersion with the agglomeration only verified at 0.7 wt % of loading. The produced AgNPs-PP film demonstrated bacteriostatic activity against *E. coli* and *S. aureus* with inhibition rates in the order of 100 and 84.6%, respectively, which was related to the Ag^+ ion release from the binary film.

Masterbatches of a polymer resin mixed with a M_0F are already found at the market, and it is a good alternative to provide homogeneous dispersion with a polymer melt, allowing enhanced polymer intrinsic properties, antimicrobial activity, gas barrier and UV–vis protection in comparison to their neat counterparts (Table 1) (Bumbudsanpharoke, Lee, & Ko, 2018; Jo et al., 2018). As alternative to the mixing methods for PM_0C film making, coating of polymer films is also a good solution to avoid the problems related to the inner dispersion heterogeneity. For example, Lin Li et al. (Li, Wang, & Zhu, 2018) (Table 1) prepared a AgNPs/MPE coating onto a PE film, resulting in an enhanced (>99%) antibacterial activity vs. *E. coli* and *S. aureus*. However, the close contact of the coating to the foodstuff may be posed as a drawback due to the related toxic effects as will be discussed in section 4.

Nowadays, concern over the environmental impact of the conventional thermoplastics has led to an increase research over biodegradable and biobased PM_0C. Solution casting is the preferred mixing strategy in order to incorporate M_0F into biodegradable polymer matrices. For example, a AgNPs-PBAT binary film incorporated with AgNPs pre-synthesized using tocopherol (Vitamin E) as reducing agent, showed bacterial reduction of *E. coli* and *L. monocytogenes* after 15 h, with improved water vapour barrier (WVB), UV–vis barrier, tensile strength and elastic modulus (Table 1) (Shankar & Rhim, 2016). Similar food packaging related improvements are verified for other biodegradable PM_0C as presented in Table 1, for PLA (Shankar, Rhim, & Won, 2018), agar (Shankar & Rhim, 2015), chitosan (Kadam, Momin, Palamthodi, & Lele, 2019; Qin, Liu, Yuan, Yong, & Liu, 2019), or blends such as gelatin/PVA (Basak, Das, Biswas, Biswas, & Mahapatra, 2018).

An alternative approach for the fabrication of binary PM_0C is by the combination of solution casting and *in situ* generation of the M_0F. That is, the polymer is mixed with the reducing agent, and by adding the metal precursor, the *in situ* generation of the M_0F occurs. For example, a biodegradable AgNPs-PPC binary film was fabricated by *in situ* generated AgNPs using tamarind seed polysaccharide (TSP) acting as both the filler and the reducing agent (Table 1) (Devi et al., 2019a).

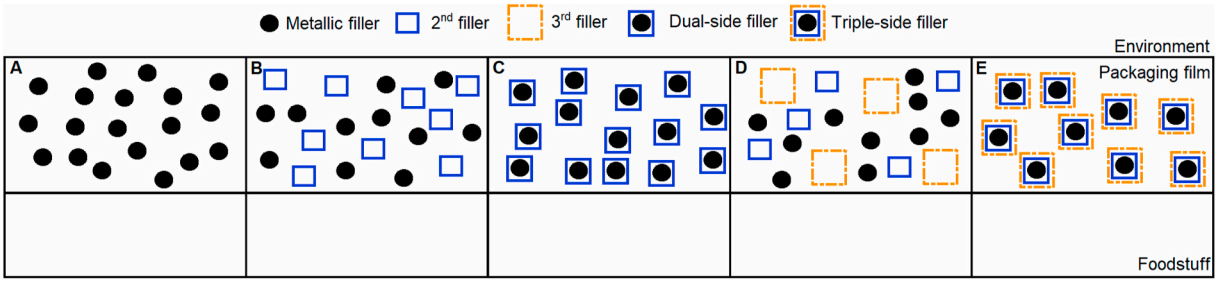

Fig. 2. Polymer-metallic composites divided as binary (A, M_0F-polymer), ternary (B, M_0F1+F2-polymer; C, M_0F1/F2-polymer), and quaternary (D, M_0F1+F2+F3-polymer; E, M_0F1/F2/F3-polymer) composite films. M_0F1 is the metallic filler, F2 and F3 correspond to the second and third added filler.

Table 1
Binary polymer-metallic composites with promising potential and already applied in food packaging.

Filler[1]	Added form; size; loading[2]	Polymer matrix (process)[3]	Polymer intrinsic properties[4]	Food packaging properties[5]	Ref.
Polymer-silver binary composites					
AgNPs	Powder; 26–41 nm; 0.1–4.0 wt%)	PP (MB film)	Enhanced THS; decreased TES	**Antimicrobial**: *P. aeruginosa*, *S. aureus*	Oliani et al. (2017)
AgNPs	Colloid w/$NaBH_4$; 7.5–11.5 nm; 0.05–0.7 wt%	PP (MB film)	Enhanced THS, SM	**Antimicrobial**: *E. coli* (100%), *S. aureus* (84.6%); **Migration** (4% AA, W, 20% EtOH, and *n*-hexane; 20, 40, 50 °C/10d; μg/cm^2): 1.8–24.5	Cao et al. (2018)
AgNPs	AgNPs-LDPE/PP masterbatches; 30–40 nm; 3–290 mg/kg	PP; LDPE (MB film)	Enhanced YM, TES, EB in LDPE; decreased YM, TES, EB in PP	**Antimicrobial**: *E. coli* (88.79–99.98%), *S. aureus* (95.17–99.97%)	Jo et al. (2018)
AgNPs	AgNPs-LDPE masterbatch; 20–50 nm; 3–240 ppm	LDPE (MB film)	Enhanced TES, EB; decreased %T, THS, C	**Antimicrobial**: *E. coli*, *S. aureus* (99.6–99.9%); **Barrier:** WVB (14.4%); OB (28.3%)	Bumbudsanpharoke et al. (2018)
AgNPs	Powder; 60–120 nm; 50, 100 ppm	PE (Coating film)	Enhanced WCA; decreased EB	**Antimicrobial**: *E. coli* (>99.98%), *S. aureus* (99.97%); **Migration** (W; 37 °C/30d; μg/l•cm^2): <0.098 (100 ppm), <0.075 (50 ppm) at 30d	Li, Li, Zhang, Yuan, and Qin (2018)
AgNPs	Colloid w/tocopherol; 10–50 nm; 0.25 wt%	PBAT (SC film)	Enhanced TES, EM, WCA; decreased EB	**Antimicrobial**: *E. coli* (~60–80%* at 15h), *L. monocytogenes* (~40–60%* at 15h); **Barrier**: WVB (~18%*); **UV–vis barrier**	Shankar and Rhim (2016)
AgNPs	Colloid w/lignin; <100 nm; 0.1, 0.5 wt %	PLA (SC film)	Enhanced TES, EM, THS; decreased %T	**Antimicrobial**: *E. coli*, *L. monocytogenes* (~100%* at 15h); **Barrier:** WVB (~17%*); **UV–vis barrier**	Shankar et al. (2018)
AgNPs	Colloid w/amino acids; 10–20 nm	Agar (SC film)	Enhanced EB, MC; decreased %T, TES, EM, THS, WCA	**Antimicrobial**: *E. coli* (~78–90%* at 15h), *L. monocytogenes* (~50–80%* at 15h); **Barrier:** WVB (~4–14%* increase); **UV–vis barrier**	Shankar and Rhim (2015)
AgNPs	Colloid w/plant extract; 2–15 nm; 0.1–0.3% w/v	Chitosan (SC film)	Enhanced TES, EB, THS, WS; decreased MC.	**Antimicrobial**: *E. coli*, *P. aeruginosa*, *B. subtilis*, *S. aureus* (~45–60%*); **Barrier:** WVB (15%); **Migration** (PB pH 5.5 and 6.8; 25 °C/10d; ppm): 0.3–1.5*	Kadam et al. (2019)
AgNPs	Powder; 60–120 nm; 2 wt%	Chitosan (SC film)	Enhanced TES; decreased EB, MC, WS	**Antimicrobial**: *E. coli*, *Salmonella*, *S. aureus*, *L. monocytogenes*; **Barrier:** WVB (~8–16% *); **UV–vis barrier; Antioxidant** properties (due to added PCE); **Intelligent Packaging**: pH sensitive colour changes (due to added PCE)	Qin et al. (2019)
AgNPs	Colloid w/plant extract; 15–80 nm	Gelatin/PVA (SC film)	–	**Antimicrobial**: *E. coli*, *S. aureus*	Basak et al. (2018)
AgNPs	*In situ* w/TSP; 44–86 nm; 1.0–5.0 mM	PPC (SC film)	Enhanced TM, TES, THS; decreased EB	**Antimicrobial**: *P. aeruginosa*, *E. coli*, *B. lichenformis*, *S. aureus*	Devi et al. (2019a)
AgNPs	*In-situ* w/UV radiation; 16–797 mg/kg (0.006–0.32 wt%)	Starch/PVA (SC film)	Enhanced EM and TES (0.006, 0.06 wt%), EB (0.16, 0.32 wt%); decreased EB (0.006, 0.06 wt%), EM and TES (0.16, 0.32 wt%), THS, MC, T	**Antimicrobial**: *L. innocua* (>80%*), *E. coli*, *A. niger*, *P. expansum* (>99%*); **Barrier:** WVB (~10–25%*); **Migration** (20 °C/7d): 3% AA: 100% at 1h; 10, 20, 50% EtOH: 100% at 4–10h; oleic acid: 50–78%	Cano et al. (2016)
AgNPs	*In situ* w/pullulan; 7 mM	Pullulan; Pullulan// Pectin (SC film)	Enhanced MC, WCA, EB; decreased %T, TES, EM	**Antimicrobial**: *E. coli*, *L. monocytogenes*, *S. typhimurium*, *S. aureus*, *B. cereus* (100%*)	Lee et al. (2019)
AgNPs	*In situ* w/gelatin; 45–180 mM (0.2–0.8 wt%)	Gelatin (SC film)	Enhanced THS; decreased TES, EB, WS	**Antimicrobial**: *S. aureus*, *E. coli*; **Barrier**: WVB (12.7% absence of TA; 13% in the presence of TA)	Menezes et al. (2019)
AgNPs	*In situ* w/banana powder; 100–200 nm; 1.0 mM	Agar (SC film)	Enhanced EB; decreased TES, EM, MC, WCA, %T.	**Antimicrobial**: *E. coli* (~100%* at 15h), *L. monocytogenes* (~57%* at 15h); **UV–vis barrier**; **Antioxidant** properties.	Orsuwan et al. (2016)
AgNPs	*In situ* w/starch-maltose; 13–20 nm; 143 ppm	Starch (SC film)	Enhanced MC, TES, EM; decreased T	**Antimicrobial**: *Salmonella* spp., *E. coli*, *S. aureus*, *Penicillium* spp.; **Barrier**: WVB (~17–50%*); **UV–vis barrier**	Ortega et al. (2019)
AgNPs	*In situ* w/lignin; <500 nm; 0.5–2.0 wt%	Agar (SC film)	Enhanced THS, TES, EM, WCA; decreased %T, WS, swelling	**Antimicrobial**: *E. coli* (~100%* at 6h), *L. monocytogenes* (~100%* at 12h); **Barrier:** WVB (~8–16%*); **UV–vis barrier**	Shankar and Rhim (2017)
AgNPs	Colloid; 10–20 nm; 0.5, 1.0 wt%	LDPE (MB film)	Decreased TES, YM, EB	**Food Application** (chicken breast fillets; 4 °C/12d): reduction in psychotropic bacteria (~17%*); enhanced oxidative stability	Azlin-Hasim et al. (2015)
AgNPs	Colloid w/plant extract; 25–45 nm; 0.05, 1.0 wt%)	Chitosan/Gelatin (SC film)	Enhanced EB; decreased TES	**UV–vis barrier**; **Food Application** (red grape; 37 °C/25d): decreased mildew, putridity and bad odour; prolonged shelf life to 14d (0.05 wt%) and 18d (0.1 wt %) vs. control (<14d in neat PE)	Kumar et al. (2018)
AgNPs	<20 nm; 1.0–3.0 wt%	PE (MB film)	–	**Food Application** (pistachio, walnut, almond, hazelnut; RT/24m): inhibited growth of TBC, coliform and moulds; reduced peroxide and aflatoxin values;	Tavakoli et al. (2017)

(*continued on next page*)

Table 1 (*continued*)

Filler[1]	Added form; size; loading[2]	Polymer matrix (process)[3]	Polymer intrinsic properties[4]	Food packaging properties[5]	Ref.
				prolonged shelf life to 20m (pistachios), 19m (almonds, 18m (hazelnuts), and 18m (walnut) vs. control (13m)	
Polymer-copper binary composites					
CuNPs	*In situ* w/$NaBH_4$; 53.28 ± 15.54 nm; 0.5–5.0 wt%	HPMC (SC film)	Enhanced TES, EB	**Antimicrobial**: *S. epidermidis*, *Streptococus A*, *S. aureus*, *B. cereus*; **Barrier**: WVB (~41–60%*); **Food Application** (minced meat, 4 °C/15d): inhibited growth of TBC vs. control	Ebrahimiasl and Rajabpour (2015)
CuNPs	*In situ* w/TNP; 47–68 nm; 1–250 mM	PPC (SC film)	Enhanced THS, EM, TES; decreased EB	**Antimicrobial:** *E. coli*, *P. aeruginosa*, *B. licheniformis*, *S. aureus*	Devi et al. (2019b)
CuNPs	Powder; 50 nm; 0.25–1.0 wt%	PP (MB film)	Enhanced T, EB, THS; decreased TES	**Antimicrobial**: *E. coli*, *S. aureus*, *Shigella castellani, B. subtilis*; **Migration** (3% AA): 6.01–7.71% (20 °C/40d); 21.6–35.1% (40 °C/35d); 27.3–53.3% (55 °C/15d); 24.8–53.1% (70 °C/48h); 6.01–24.8 (0.25 wt%); 6.4–35.6% (0.5 wt%); 7.75–53.1% (1.0 wt%)	Jiang et al. (2019)
CuNPs	Powder; 50 nm; 0.5–3 wt.%	LDPE (SC film)	Enhanced THS, TES, EB	**Antimicrobial**: *E. coli*, *S. aureus*; **Barrier**: WVB (~69%* at 3 wt%); **Food application** (Peda; RT/8d): reduced microbial count (~16%* at 3 wt%); prolonged shelf life to 8d vs control (6d); **Migration** (W; 30d; mg/cm^2): 5–15* (0.5, 1 wt%); 35–40* (1.5 wt %); 65–70* (2 wt%); 75–80 (2.5 wt%); 85–90* (3 wt%)	Lomate et al. (2018)
CuNPs	*In situ* w/leaf extract; 10–60 nm; 5–250 mM	Cellulose (SC film)	Decreased THS	**Antimicrobial:** *E. coli*	Muthulakshmi et al. (2017)
CuNPs; CuMPs	Powder; 10 nm; 45 μm; 1.0, 5.0 vol%	PP; PA6; PPC18; HDPE (MB film)	Enhanced EM	**Antimicrobial**: *S. aureus*, *P. aeruginosa*; **Migration** (W; μg/(mL*cm^2)): ~2.5–3.0* w/PA6; ~1.75–2.0* w/PPC18; ~1.25–1.5* w/PP; ~0.75–1.0 w/HDPE	Palza et al. (2015)
Polymer-other metallic binary composites					
PdNPs	1.04 nm	PET (Coating film)	–	**Food application** (cooked cured ham; 4 °C/21d in normal atmosphere (~20.95 vol% O_2) or w/MAP (2 vol% O_2, 5 vol% H_2, 93 vol % N_2): 100% scavenging at 35 min of 2 vol% (MAP experiment); effective prevention in the decolorization of ham; prolonged shelf-life of 21d vs. control	Hutter et al. (2016)
PdNPs	Powder; <25 nm; 1 wt %	PHB; PCL (Electrospinning compressed film)	Enhanced THS	**Barrier**: WVB (~98.7% for paper/PHB film/PCL-PdNPs film); OB (~81% at 3000 min, 50% RH for paper/PHB fibers/PCL-PdNP and paper/PHB-PdNPs fiber/PCL-PdNPs film; ~100% at 1250 min, 50% RH for PCL-PdNPs)	Cherpinski et al. (2018)
PdNPs	Powder; <25 nm; 1 wt %	PHB (Electrospinning compressed film)	Enhanced THS, TES, and EM	**Barrier**: OB (~30% at 16.5h, 100% RH)	Cherpinski et al. (2019)
Ag-CuNPs	Powder; <100 nm; 2.0, 4.0 wt%	PLA/PEG (MB film)	Enhanced C	**Antimicrobial**: *S. typhimurium*, *L. monocytogenes*, *C. jejuni* (all ~25–64%* for Ag–Cu/PLA, ~77–100%* for Ag–Cu/CEO/PLA); **Barrier**: WVB (~41%* at 4 wt %), OB (~39%* at 4 wt%); **UV–vis barrier**; **Food application** (contaminated chicken meat; 4 °C/21d): decreased microbial count; below LOD at the 21st day for *S. typhimurium* and *C. jejuni*	Ahmed, Arfat, et al. (2018)
Ag-CuNPs	Powder; <100 nm; 0.5–4.0 wt%	LLDPE (MB film)	Enhanced C	**Antimicrobial**: *S. typhimurium*, *L. monocytogenes*, *C. jejuni* (all ~60–100%*); **Barrier:** WVB (~75%* at 4 wt%), OB (~31%* at 4 wt%); **UV–vis barrier**; **Food application** (contaminated chicken meat; 4 °C/21d): decreased microbial count; below LOD at the 14d and 7d for *S. typhimurium* and *C. jejuni*; >70% at 21d for *L. monocytogenes*	Ahmed, Mulla, et al. (2018)
Ag-CuNPs	Powder, <100 nm; 0.5–2.0 wt%	Guar gum (SC film)	Enhanced TES, THS, thermal conductivity, thermal diffusivity; decreased EB, T	**Antimicrobial**: *S. typhimurium* (~20–52% *), *L. monocytogenes* (~10–36%*); **Barrier**: OB (56.1% at 2.0 wt%); **UV–vis barrier**	Arfat, Ejaz, Jacob, and Ahmed (2017)
Ag-CuNPs	Powder, <100 nm; 0.5–4.0 wt%	Agar (SC film)	Enhanced TES, THS, C; decreased EB, T	**Antimicrobial**[c]: *S. typhimurium* (~34-7–66.4%*), *L. monocytogenes* (~21–54.7% *); **Barrier**: OB (54.01% at 4 wt%); **UV–vis barrier**	Arfat, Ahmed, and Jacob (2017)

(*continued on next page*)

Table 1 (*continued*)

Filler[1]	Added form; size; loading[2]	Polymer matrix (process)[3]	Polymer intrinsic properties[4]	Food packaging properties[5]	Ref.
SeNPs	Colloid w/AA; 50–60 nm; 10 wt%	PET-PUR-LDPE multilayer film (Solution mixing w/PUR adhesive)	–	**Antioxidant** properties (~69%* max. antioxidant capacity); **Migration** (50% EtOH, 3% AA, hazelnuts; 60 °C/10d): <LOD	Vera et al. (2016)
AuNPs	Colloid w/sodium citrate; <3 μm in film; 0.85 wt%)	PVA (SC film)	Enhanced TES, YM, THS; decreased EB, WS	**Antimicrobial:** *E. coli*; **Barrier**: WVB (~10%*); **Food application** (bananas, RT/5d): enhanced preservation up to 5d vs control	Chowdhury et al. (2020)
AuNPs	Colloid w/$NaBH_4$; 5.5 ± 1.4 nm; 2.5, 5% v/v	Starch (SC film)	Enhanced TES; decreased EB, WS, %T	**Antimicrobial**: *S. aureus* (98%), *E. coli* (99.9%); **Barrier**: WVB (~14–18%*), OB and CO_2B below LOD; **UV–vis barrier**	Pagno et al. (2015)

([1]) AgNPs (silver nanoparticles); CuNPs (copper nanoparticles); CuMPs (copper microparticles); PdNPs (palladium nanoparticles); Ag-CuNPs (silver-copper bimetallic nanoparticles); SeNPs (selenium nanoparticles); AuNPs (gold nanoparticles). ([2]) $NaBH_4$ (sodium borohydride); TSP (tamarind seed polysaccharide); TNP (tamarind nut powder). ([3]) HDPE (high-density polyethylene); HPMC (hydroxypropyl methylcellulose); LDPE (low-density polyethylene); LLDPE (linear low-density polyethylene); PP (polypropylene); PE (polyethylene); PS (polystyrene); PBAT (poly(-butylene adipate-*co*-terephthalate)); PLA (polylactic acid); PVA (polyvinyl alcohol); PPC (polypropylene carbonate); PHB (poly(3-hydroxybutyrate)); PHBV (poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)); PA6 (polyamide 6 or nylon 6); PPC18 (propylene-1-cooctadecene copolymer); PCL (polycaprolactone); PET (polyethylene terephthalate); PEG (polyethylene glycol); PUR (polyurethane); MB (melt blending); SC (solution casting). ([4]) SM (storage modulus); TES (tensile strength); YM (Young's modulus); EB (elongation at break); C (crystallinity); THS (thermal stability); EM (elastic modulus); MC (moisture content); WS (water solubility); WCA (water contact angle); %T (% transmittance); T (transparency). ([5]) (*) (approximation of the reduction values based on each literature results); *Pseudomonas aeruginosa* (*P. aeruginosa*); *Staphylococcus aureus* (*S. aureus*); *Escherichia coli* (*E. coli*); *Listeria monocytogenes* (*L. monocytogenes*); *Bacillus subtilis* (*B. subtilis*); *Bacillus lichenformis* (*B. lichenformis*); *Listeria innocua* (*L. innocua*); *Aspergillus niger* (*A. niger*); *Penicillium expansum* (*P. expansum*); *Salmonella typhimurium* (*S. typhimurium*); *Bacillus cereus* (*B. cereus*); *Staphylococcus epidermidis* (*S. epidermidis*); *Campylobacter jejuni* (*C. jejuni*); AA (acetic acid); W (water); EtOH (ethanol); PB (phosphate buffer); WVB (water vapour barrier); OB (oxygen barrier); CO_2B (carbon dioxide barrier); PCE (purple corn extract); TA (tannic acid); RT (room temperature); TBC (total bacterial count); MAP (modified atmosphere packaging); LOD (limit of detection).

Antimicrobial activity against *E. coli*, *P. aeruginosa*, *B. licheniformis* and *S. aureus* was verified, accompanied with enhanced tensile strength, thermal stability and storage modulus. Several other studies adopted this strategy as presented in Table 1 for *in situ* generated M_0F in a starch/PVA (Cano, Cháfer, Chiralt, & González-Martínez, 2016), pullulan and pullulan/pectin (Lee, Jeong, & Kanmani, 2019), gelatin (Menezes et al., 2019), agar (Orsuwan, Shankar, Wang, Sothornvit, & Rhim, 2016; Shankar & Rhim, 2017), and starch (Ortega, García, & Arce, 2019) films.

Polymer-silver binary composite films have also been tested with real food systems to determine their effectiveness on food shelf life extension. For instance, a AgNPs-LDPE film was tested to serve as potential food packaging option for chicken breast fillets (Table 1) (Azlin-Hasim, Cruz-Romero, Morris, Cummins, & Kerry, 2015), resulting in growth inhibition of psychotropic bacteria accompanied with an enhanced oxidative stability compared to a LDPE control film. Other studies of AgNPs-polymer binary films (Table 1) resulted in the shelf life extension of red grapes (18 days vs. <14 days in control film) and dry fruits (18–20 months vs. 13 months in control film) (Kumar, Shukla, Baul, Mitra, & Halder, 2018; Tavakoli, Rastegar, Taherian, Samadi, & Rostami, 2017).

Polymer-copper binary composites. Copper-based fillers have long been used to reinforce polymer matrices (Tamayo et al., 2016). It is an economically cheaper metal as compared to others like gold, silver, or platinum, making it very promising for industrial-scale applications. The incorporation of copper-based fillers has leaded to the generation of PM_0C with enhanced properties, suitable to be applied as food packaging options, as presented in Table 1.

As examples of copper-based binary films applied in real food packaging, a CuNPs-LDPE film (Table 1) was used to store Peda (Indian sweet dairy product) (Lomate, Dandi, & Mishra, 2018). The CuNPs-LDPE film exhibited antimicrobial activity that was associated to the release of copper ions, allowing the shelf life extension of Peda up to 8 days in comparison with the control LDPE film, where Peda started to degrade at the 6th day. This film was prepared by mixing pre-synthesized CuNPs using a microwave assisted method with the LDPE polymer solution. In another study, a CuNPs-HPMC binary film showed potential for food packaging due to the increased antimicrobial activity, gas barrier properties, and the inhibition of the total bacteria count in a packed sample of minced meat (Table 1) (Ebrahimiasl & Rajabpour, 2015).

Polymer-other metallic binary composites. Metal-based scavengers inside a polymeric matrix can act both as physical (through the tortuous path effect) and active barrier (through chemical reactions) to scavenge the permeating and inner package oxygen, protecting the food against oxygen-induced problems, and thus extending the shelf life. For example, in a melt blended PP composite film filled with ~20 wt% of an iron-based oxygen scavenger powder (SHELFPLUS® O2 2710 with an oxygen absorption capacity of 44 mg O_2 per g of additive after 30 days), a capacity of 48.6 mg/g of oxygen absorbed was reached (Lehner, Schlemmer, & Sängerlaub, 2015).

The use of zero valent iron nanopowders seems an interesting alternative to common iron micropowders, since their scavenging activity is much bigger due to their high surface area, and their activation is already noticed at dry conditions (Foltynowicz, Bardenshtein, Sängerlaub, Antvorskov, & Kozak, 2017; Mu et al., 2013). According to Foltynowicz et al. (Foltynowicz et al., 2017), the oxygen scavenge rate of nanoscale iron (10 nm) was 2–3 times higher at 100% relative humidity (RH) than non-nanoscale iron (212 μm). The same authors also mechanically mixed the nanoscale iron in a silicon matrix, observing that the uptake of oxygen was more than 10 times faster than certain commercial films consisted of PE and PP filled with micron-sized iron powders.

Besides iron-based oxygen scavengers, palladium nanoparticles (PdNPs) are noticed as another alternative to scavenge oxygen. PdNPs in the presence of hydrogen can remove residual oxygen by catalysing the oxidation of hydrogen into water (Hutter, Rüegg, & Yildirim, 2016). Cherpinski et al. (Cherpinski, Gozutok, Sasmazel, Torres-Giner, & Lagaron, 2018) prepared an oxygen scavenging film of poly (3-hydroxybutyrate) (PHB) containing PdNPs (Table 1). The films presented an oxygen scavenging capability of ~30% for a final time of 16.5 h at 100% RH, accompanied with improved thermal stability and mechanical properties.

The same authors developed biodegradable coatings consisted of PHB and polycaprolactone (PCL) filled with PdNPs for oxygen scavenging purposes (Table 1), using a cellulose-based packaging (*e.g.*, paper) as support substrate for the coatings (Cherpinski, Szewczyk, Gruszczyński, Stachewicz, & Lagaron, 2019). All the prepared multilayer systems exhibited oxygen scavenging at 50% RH with the best

systems being the paper/PHB-fibers/PdNPs-PCL-film and paper/PdNPs-PHB-fiber/PdNPs-PCL-film with ~81% reduction at 3000 min for both systems. The oxygen scavenging capability of the PdNPs was enhanced by the incorporation of the PCL matrix, which is a more oxygen permeable material than PHB. This was supported by the excellent oxygen scavenging ability of the PdNPs-PCL film with a ~100% oxygen depletion at 1250 min at 50% RH.

PdNPs coated on a PET film by magnetron sputtering technology was tested to preserve the colour of cooked cured ham (Table 1) (Hutter et al., 2016). This film allowed the scavenging of the all the oxygen within 35 min, leading to a prolonged shelf life of 21 days by preventing the decolorization of the ham. Control samples (without PdNPs) showed increased decolorization within 2 h of storage. However, the oxygen scavenging capability of PdNPs is highly dependent on the hydrogen concentration in the package to promote the catalysis reaction. Recently, a review article pointed out the use of multiple metallic inorganic fillers, including iron powder, activated iron, ferrous oxide, iron salt, Co(II), zinc, and others, to be applied as oxygen scavengers in polymer films (Gaikwad et al., 2018).

Bimetallic particles are also efficient M_0F with excellent antimicrobial and UV–vis protection properties, and thus, their application to produce PM_0C for food packaging applications has been performed and is represented in Table 1. For example, a PLA film filled with bimetallic silver-copper nanoparticles (Ag-CuNPs) in addition with cinnamon essential oil (CEO), was tested to serve as food package for chicken meat samples contaminated with *S. typhimurium, L. monocytogenes,* and *C. jejuni* bacteria (Table 1) (Ahmed, Arfat, et al., 2018). The developed films presented reduced the WVB and oxygen barrier (OB), enhanced UV–vis protection, and antibacterial activity by observing a decrease in the counts of *C. jejuni* and *S. typhimurium* in the contaminated chicken meat samples, which reached below the detection level on the 21st day, and with less activity against *L. monocytogenes*.

Additional M_0F with potential to be included in polymer matrices for food packaging applications are the selenium nanoparticles (SeNPs). These are known as synthetic antioxidants due to their free radical scavenging capability, that can serve to produce SeNPs-polymer composite films with antioxidant activity to reduce the oxidation and early maturation of the packaged food (Table 1) (Vera et al., 2016). Furthermore, the use of gold as metallic filler has showed promissing food packaging related properties, such as antimicrobial activity, reduced WVB and OB, and enhanced UV–Vis protection (Table 1) (Chowdhury, Teoh, Ong, Zaidi, & Mah, 2020; Pagno et al., 2015). In a real food application, a AuNPs-PVA binary film enhanced the shelf life (up to 5 days) of packed bananas in comparison to the control film (Table 1) (Chowdhury et al., 2020).

3.2. Ternary and quaternary polymer-metallic composites

Ternary composites (M_0F1/F2). This type of PM_0C involves adding dual-side fillers into a polymer matrix, leading to ternary M_0F1/F2-polymer composites. Some examples of dual-side fillers (M_0F1/F2) used to form ternary composites with potential as food packaging are summarised in Table 2.

As representative example of a ternary M_0F1/F2-polymer composite applied as food packaging, an AgNPs/BNC dual-side filler was produced by incorporating AgNPs into bacterial nanocellulose (BNC) by chemical and UV-assisted reduction of the Ag^+/BNV slurry. This was later used to produce a AgNPs/BNC-PVA composite by solution casting (Wang et al., 2020). This ternary film allowed enhanced WVB and OB properties, and inhibition in the growth of bacteria in packed raw beef (Table 2).

In another example, an AgNPs/Laponite dual-side filler synthesized by the reduction of an Ag^+/Laponite mixture with the use of quaternized chitosan as green reductant, was used to produce an AgNPs/Laponite-Chitosan ternary composite by solution casting (Wu, Huang, Li, Xiao, & Wang, 2018). Improved mechanical, WVB, OB and water solubility properties were detected, and mainly related to the addition of the laponite. On the other hand, the observed antimicrobial activity was related to the presence of the AgNPs. This synergistic effect between laponite and the AgNPs in the AgNPs/Laponite-Chitosan composite, allowed an extension in the shelf life of litchi fruits by 7 days in comparison to the control PE and chitosan (5 days) (Table 2).

Ternary composites (M_0F1+F2). The manufacture of ternary PM_0C can also be made by the addition of the second filler separately from the M_0F (*i.e.*, there is no pre-synthesized chemical and/or physical attachment between the fillers), and some examples are presented in Table 2. Taking a FeNPs+OMMT-PP ternary composite film as representative example, the synthesis of this ternary film involved the separate mixing of the clay powder and the iron nanoparticles with the polymer granules (polypropylene), later processed in a twin extruder to give the FeNPs+OMMT-PP film (Khalaj, Ahmadi, Lesankhosh, & Khalaj, 2016). This composite provided enhanced barrier properties, achieving reduced values in WVB (max. of ~77%) and OB (max. of ~55%) *vs*. neat PP control film (Table 2).

Several studies were grouped in Table 2 in which ternary M_0F1+F2 composites are applied to real food packaging. For instance, a PLA ternary composite film filled with TiO_2, AgNPs, and bergamot essential oil (BEO) was used to fabricate AgNPs+TiO_2+BEO-PLA films (Table 2) that allowed to maintain the quality of fresh mango for 15 days, by obtaining superior results in terms of colour, total acidity, vitamin C, weight loss, and microbial content when compared to neat PLA and BEO-PLA films (Chi et al., 2019). Other studies evidenced food preservation using AgNPs+MMT-PVA films in the package of chicken sausage (Mathew, S, Mathew, & Radhakrishnan, 2018), AgNPs+GST-Chitosan film in the storage of wheat bread slices (Nair, Alummoottil, & Moothandasserry, 2017), and AgNPs+TiO_2-PLA film in the package of cottage cheese (Li, Zhang, et al., 2017), leading to prolonged shelf life in comparison to control films, as given in Table 2.

Quaternary composites (M_0F1/F2/F3). The development of new and alternative fillers, such as triple-side fillers (M_0F1/F2/F3, where M_0F is the metallic filler 1, F2 is filler 2, and F3 is filler 3) has led to the manufacture of quaternary composite films as represented in Table 2, applied for food packaging (Biswas, Tiimob, Abdela, Jeelani, & Rangari, 2019; Naskar et al., 2018; Vasile et al., 2017). As a representative example, a silver-carbon-silica (AgNPs/Carbon/SiO_2) triple-side filler was synthesized by doping a carbon-silica hybrid obtained from rice husk pyrolysis with AgNPs produced through a ball-milling process (Biswas et al., 2019). This filler was used to produce an AgNPs/Carbon/SiO_2-PBAT quaternary film that displayed antimicrobial action, for which the authors suggested its potential use in food packaging applications (Table 2). However, poor interaction between the polymer and the triple-side filler was evidenced, causing a decrease in the mechanical proprieties in comparison to the neat control film.

Quaternary composites (M_0F1+F2+F3). Quaternary composite films by the separate addition of multiple fillers (M_0F1+F2+F3) has also led to the formation of PM_0C with potential use in food packaging, and some examples are displayed in Table 2. In the study from Li et al. (Table 2) (Li, Zhang, et al., 2017), the separate mixing of a AgNPs/TiO_2 nanopowder, silica, and attapulgite (clay) with a LDPE/LLDPE melt blend was performed to prepare a masterbatch. The masterbatch pellets were latter used in combination with LDPE to prepare the AgNPs/TiO_2+SiO_2+Attapulgite-LLDPE/LDPE quaternary films by a plastic extruder; latter transformed into bags using a heat sealer. An XRD (powder X-ray) analysis of the composite film evidenced the presence of TiO_2 phases with no presence of Ag phase, suggesting their low particle size (less than 3 nm). This composite was used for the storage of rice and displayed inhibition in the microorganism growth, maintenance of the rice texture (hardness, springiness, and adhesiveness), and a slow aging of the rice, in comparison to neat PE package bags as control.

An analogous system was also applied to mushrooms preservation as presented in Table 2 (Donglu et al., 2016). Few more examples are given in Table 2. A quaternary composite film composed of Ag, ZnO and CuO nanoparticles melt blended with LDPE was used for the storage of

Table 2
Ternary/quaternary polymer-metallic composites with promising potential and already applied in food packaging.

Filler (added form; size; loading)[1]	Polymer matrix (process)[2]	Polymer intrinsic properties	Food packaging properties[3]	Ref.
Ternary (M_0F1/F2) composite films				
AgNPs/TiO_2 (powder; <70 nm; 1.0–5.0 wt%)	LDPE (MB film)	Enhanced TES; decreased EB	**Antimicrobial**: *E. coli* (70–95%), *S. albidoflavus* (70–85%)	Nasab, Jalili, and Farrokhpay (2018)
AgNPs/TiO_2 (powder; 10 nm AgNPs; 3.0, 5.0 wt%)	LDPE (MB film)	–	**Food Application** (mazafati dates: 50, 20, 8, 4 °C/53d; pistachio: 50, 25, 0, −18 °C/8d): enhanced acidity, pH, TSS, reducing sugars (in dates), and texture (in pistachios); prolonged shelf life of dates (by 53d) and pistachio (by 8d) vs. control (LDPE)	Mousavi, Pour, Nasab, Rajabalipour, and Barouni (2015)
AuNPs/TiO_2 (powder; 45 nm AuNPs; 2.5 wt%)	SA (SC film)	Enhanced WCA, polymer degradation	**Antimicrobial:** *E. coli* (~87–100%*), *S. aureus* (~90–100%*)	Tang et al. (2018)
AgNPs/Kaolinite (powder; 5–60 nm AgNPs; 2.0–5.0 wt%)	PCL (SC film)	–	**Antimicrobial**: *S. aureus*, *E. coli* (100%*); **Barrier**: OB (52–69%), WVB (52–66%); **Migration** (HNO_3; RT/40d; mg/kg*cm^2): <0.018	Benhacine, Ouargli, and Hadj-Hamou (2019)
AgNPs/OMMT (powder; 2–35 nm AgNPs; 3.0, 5.0 wt%)	CA/TEC (SC film)	Enhanced THS, TES, EM; decreased %T, EB	**Antimicrobial**: *E. coli, P. aeruginosa, S. enterica, S. aureus*; **Barrier**: OB (~8–14%*); **Antioxidant properties** (by added thymol at 4.0, 8.0 wt%); **UV–vis barrier**	Dairi, Ferfera-Harrar, Ramos, and Garrigós (2019)
AgNPs/Laponite (<100 nm, <50 nm AgNPs; 5 wt%)	Chitosan (SC film)	Enhanced TES, tensile strain; decreased swelling, WS	**Antimicrobial**: *S. aureus, E. coli, A. niger, P. citrinum*; **Barrier**: WVB (17–30%*), OB (98–100%*); **Food application** (fresh litchi fruits; 25 °C/7d at 75% RH): prolonged shelf life by 7d vs 5d neat PE and chitosan films; **Migration** (TRIS-HCl buffer pH 7.4; 25 °C/74h): 5.6% (AgNPs/Laponite-Chitosan); 29.1% (AgNPs-Chitosan)	Wu et al. (2018)
AgNPs/Eggshell (powder; 10–15 nm AgNPs; 0.5–2.0 wt% [0.23–1.15 ppm Ag])	PBAT/PLA (MB 3D printed film)	Enhanced THS, C; decreased TS, toughness	**Antimicrobial**: *S. enteritidis, L. monocytogenes*; **Migration** (W at 4 °C, 50 °C/72h, chicken breast at 4 °C/164h): ND	Tiimob et al. (2017)
AgNPs/Alginate microbeads (powder; 190 μm; 10–20 nm AgNPs; 5 wt% [0.20 mg/g Ag])	PLA (SC film)	Enhanced YM; decreased EB, failure strain	**Antimicrobial**: *S. aureus*; **Migration** (mg/kg): W, 95% EtOH: 0.011–0.041 (4 °C, 20 °C, 40 °C/10d); 3% AA: 0.13 ± 0.05 (20 °C/10d)	Kostic, Vukasinovic-Sekulic, Armentano, Torre, and Obradovic (2019)
CuNPs/Cellulose (powder; 0.2% w/v)	SA-P/C (SC film)	Enhanced THS, TES; decreased EB, WS, T	**Antimicrobial**: *E. coli;* **Barrier**: WVB (~52%*); **UV–vis barrier**; **Food application** (coconut oil; 35 °C/90 d at 53% RH): reduced oxidation rate; prolonged shelf life by 90d	Gautam and Mishra (2017)
AgNPs/BNC (20–30 nm AgNPs; 5 wt %)	PVA (SC film)	Enhanced EB; decreased TES	**Antimicrobial:** *E. coli* (max. 7.3 log CFU/L reduction); **Barrier**: WVB (~28%*), OB (~40%*); **Food application** (normal round beef; *E. coli* spiked round beef; 4 °C/14d): reduction in bacteria in normal round beef (max. of 3 log CFU/cm^3 at day 7); reduction of *E. coli* in spiked beef (max. of 3 log CFU/cm^3 at day 10); number of *E. coli* 1 log CFU lower during two weeks; **Migration** (saline solution, 37 °C/168h, mg/m^2): max. of 5–7 at 168h	Wang et al. (2020)
Ternary (M_0F1+F2) composite films				
AgNPs (<150 nm; 1 wt%) + TiO_2NPs (<100 nm; 2 wt%)	PLA (SC film)	–	**Food application** (fresh mango; RT/15d): improved values of colour, total acidity, vitamin C, weight loss, and microbial content; prolonged shelf life by 15d vs. control (<15d for neat PLA and BEO-PLA films)	Chi et al. (2019)
AgNPs (20 ± 15 nm; 2.5–7.5 wt%) + SeNPs (50 ± 15 nm; 2.5–7.5 wt %)	FUR/Gelatin (SC film)	Enhanced EM, density, WC, swelling, TES, EB; decreased WS	**Antimicrobial**: *E. coli*, *S. aureus*, MRSA**; Barrier:** WVB (~2%*)**; Food application** (kiwi fruits; RT/8d)**:** reduced weight loss; extension of shelf life by 8d vs. control (6d)	Jamróz et al. (2019)
FeNPs (colloid; 50–70 nm; 0.05–0.2 wt%) + OMMT (powder; 1.0–4.0 wt%)	PP (MB film)	Enhanced EM, TES; decrease EB	**Barrier**: WVB (~0–77%*) and OB (~24–55%*); **Migration** (cheese water; 10d): 0.3–1.04 mg/kg (Fe); 0.053–0.06% (OMMT)	Khalaj et al. (2016)
AgNPs (powder; 10 nm; 1 wt%) + TiO_2 (powder; <100 nm; 2 wt%)	PLA (SC film)	–	**Food Application** (Yunnan cottage cheese; 5 °C/25d): inhibited growth of total bacterial count, yeasts and moulds; enhanced pH, LAB (lactic acid bacteria count), sensory quality, antimicrobial activity vs. PLA and LDPE control films; prolonged shelf life to 25d vs. control (15d for LDPE and 20d for PLA); **Migration** (μg/kg): **hexane**: 127.38 (Ti); 135.58 (Ag) (40 °C/25d); **cottage cheese**: 12.27 ± 2.30 (Ti); 20.04 ± 1.38 (Ag) (5 °C/25d)	Li, Li, et al. (2018)
AgNPs (powder; 10 nm; 0.5 wt%) + TiO_2 (powder; <100 nm; 1.0, 5.0 wt%)	PLA (SC film)	Enhanced EM, EB, C, THS, opacity; decreased TES.	**Antimicrobial**: *E. coli* (51–66%*), *L. monocytogenes* (55–63%*); **Barrier**: WVB (~13–29%*); **Migration** (25 °C/40d; μg/kg): 50% EtOH: 0.72–0.99 (Ti); 0.8–0.9 (Ag); 3% AA: 2.36–3.5 (Ti); 2.8–3.3 (Ag)	Li, Zhao, et al. (2017)
AgNPs (*in situ* w/ginger extract) + MMT (powder; 25 wt%)	PVA (SC film)	Enhanced TES, YM; decreased EB, water absorption, MC, WS, water holding capacity, T	**Antimicrobial**: *S. typhimurium* (~100%*), *S. aureus* (~60%*); **UV–vis barrier; Food Application** (chicken sausage, 4 °C/4d): inhibition of bacterial growth vs. LDPE control	Mathew, S, Mathew, and Radhakrishnan (2019)

(*continued on next page*)

Table 2 (*continued*)

Filler (added form; size; loading)[1]	Polymer matrix (process)[2]	Polymer intrinsic properties	Food packaging properties[3]	Ref.
AgNPs (*in situ* w/starch) + MMT (powder; 25 wt%)	PVA/Starch (SC film)	Enhanced TES, YM; decreased EB, water absorption, MC, WS, water holding capacity	**Antimicrobial**: *S. typhimurium, S. aureus* (both ~100%*); **UV–vis barrier**	Mathew et al. (2018)
AgNPs (colloid w/starch; 5 nm; 3 mL) + GST (0.5–1.5 g)	Chitosan (SC film)	Enhanced TES, WCA; decreased EB, swelling, WS, MC	**Antimicrobial**: *S. aureus, E. coli. C. albicans*; **Barrier:** OB (~57%*), WVB (~54%*); **Food Application** (wheat bread slices, 35 °C/14d): inhibited growth of bacteria count (7.13–3.84 log CFU/g reduction) vs. control film (19.17 log CFU/g); prolonged shelf life to 8-10d vs. control (4d); **Migration** (wheat bread slices; 40 °C/14d; μg/L): 2.8–3.2 (7d), 3.7–3.9 (10d), 4.4–4.5 (14d)	Nair et al. (2017)
AgNPs (powder; 35–50 nm; 1.0 wt %) + BCNC (powder; 20–30 nm; 2.0–6.0 wt%)	Chitosan (SC film)	Enhanced TES, EM, C, THS, WCA; decreased EB, MC, WS	**Antimicrobial**: *S. aureus, B. cereus, E. coli, P. aeruginosa, C. albicans*; **Barrier**: WVB (~9–26%*); **UV–vis barrier**	Salari, Khiabani, Mokarram, Ghanbarzadeh, and Kafil (2018)
AgNPs (colloid w/starch; 16–20 nm; 1.0–7.0 wt%) + NC (240–280 nm; 4.0–16.0 wt%)	PVA (SC film)	Enhanced breaking stress, EB, TES, THS	**Antimicrobial**: *S. aureus, E. coli*; **Barrier**: WVB (~17–62%*)	Sarwar et al. (2018)
AgNPs (colloid w/plant extract; 20 μg) + Laponite (powder; 1.0–7.0 wt%)	PP (Coating film)	–	**Antimicrobial**: *E. coli, S. aureus*; **Barrier**: OB (~52% *), WVB (~50%*); **Migration** (μ/L): 7.4 **(-2°C)**; 7.7 (0 °C)	Vishnuvarthanan and Rajeswari (2019)
AgNPs (UV-radiation; 25.7–56.6 nm; 2–8 mL $Ag(NH_3)_2(OH)$ 1 M) + CNFs (15 ± 5 nm; 10 wt%)	PLA (Coating film)	Enhanced C, THS, TES, YM; decreased EB, water uptake	**Antimicrobial**: *S. aureus, E. coli*; **Barrier**: WVB (max. ~60.1%); **UV–vis barrier**; **Migration** (overall migration; mg/kg): 10% EtOH: <10 (40 °C/10d), 3.4–46 (40 °C/72h); isooctane: <12 (20 °C/2d); specific migration: 3.4–46 μg/kg Ag (10% EtOH)	Yu, Yang, Lu, Chen, and Yao (2016)
Quaternary (M_0F1+F2+F3 or M1/F2/F3**) composite films**				
SiO_2/Carbon/AgNPs (15–100 nm SiO_2; <100 nm AgNPs; 0.5–1.5 wt%)	PBAT (SC 3D printed film)	Enhanced THS; decreased mechanical properties.	**Antimicrobial**: *S. enteritidis*; **Migration** (W, chicken breast; 4 °C/4w): ND	Biswas et al. (2019)
AgNPs/ZnO/rGO (14–19 nm ZnO; 28–35 nm AgNPs; 1.0, 3.0 wt%)	Agar (SC film)	Enhanced TES; decreased EB	**Antimicrobial**: no microbial growth in the agar composite film for 90d	Naskar et al. (2018)
Ag/Cu/ZnO (powder; 15–24 nm; 0.5–1.5 wt%)	PLA (MB film)	Enhanced C, EB; decreased TES, YM	**Antimicrobial**: *P. aeruginosa* (82–99%*); **Barrier**: WVB (~29%*), CO_2B (~74%*), OB (~93%*); **UV–vis barrier**; **Migration** (70 °C/2h; mg/dm^2): Zn: 0.248–1.725 (W); 0.684–3.159 (10 EtOH); 0.613–4.550 (3% AA); Cu: 0.005–0.011 (W); 0.005–0.185 (10% EtOH); 0.040–0.093 (3% AA); Ag: 0.001–0.001 (W, 10% EtOH, 3% AA)	Vasile et al. (2017)
AgNPs + CuONPs + ZnONPs (35; 50; 20–30 nm; 0.167–1 wt.%)	LDPE (MB film)	–	**Food Application** (cheese samples, 4 °C/4w): reduced coliform bacteria (max. 4.21 log CFU/g reduction) vs. control LDPE (1.04 CFU/g reduction)	Beigmohammadi et al. (2016)
AgNPs + TiO_2NPs + Attapulgite + SiO_2NPs (combined powder; 40–60 nm; 15 wt% [38.12–40.21 mg/kg Ag])	LDPE/LLDPE (MB film)	Enhanced longitudinal strength	**Barrier**: OB (8.0%), WVB (10.5%); **Food Application** (mushrooms; 4 °C/14d; 90–95% RH): enhanced sensory attributes; respiration rate and weight loss inhibition; retention of vitamin C, proteins, and total soluble solids; prolonged shelf life vs. control (LDPE); **Migration** (mushrooms; 4, 25 °C/14d): not statistically significant	Donglu et al. (2016)
AgNPs/TiO_2 (powder; <3 nm AgNPs; 9.0 g [17.59 mg/kg Ag]) + Attapulgite (4.5 g) + SiO_2 (1.5 g)	LDPE/LLDPE (MB film)	–	**Antimicrobial**: *A. flavus* (~92%); **Food application** (rice; 37 °C/1m; 70% RH): growth inhibition of mildew (~23%); enhanced quality (texture and pasting properties); reduced microbial population; slow aging vs. control (neat PE); **Migration** (mg/kg): 3% AA: 0.0161–0.0255 (37 °C/6d), 0.0193–0.0371 (50 °C/12h); 10% EtOH: ND (37 °C/6d; 50 °C/12h); Rice: 0.003–0.008 (37 °C/35d)	Li, Zhao, et al. (2017)

(1) TiO_2 (titanium dioxide); OMMT (organically modified montmorillonite clay); BNC (bacterial nanocellulose); MTT (montmorillonite clay); GST (cassava starch granules); BCNC (bacterial cellulose nanocrystals); NC (nanocellulose); SiO_2 (silicon dioxide); ZnO (zinc oxide); rGO (reduced graphene oxide); CuONPs (copper oxide nanoparticles); **(2)** SA (sodium alginate); CA/TEC (cellulose acetate/triethyl citrate); SA-P/C (sodium alginate-pectin/casein); FUR (furcellaran); **(3)** *Streptomyces albidoflavus* (*S. albidoflavus*); *Salmonella enterica* (*S. enterica*); *Penicillium citrinum* (*P. citrinum*); *Salmonella enteritidis* (*S. enteritidis*); MRSA (multi resistant *Staphylococcus aureus*); *Candida albicans* (*C. albicans*); *Aspergillus flavus* (*A. flavus*); ND (not detected) TSS (total soluble solids).

cheese, leading to a reduction in coliform bacteria in comparison to a LDPE control (Beigmohammadi et al., 2016). The improvement of the food packaging-related properties and the polymer intrinsic properties is clearly observed when a M_0F is added in complementation to other fillers due to the synergistic effect. This effect is exactly the purpose behind the addition of the fillers separately (M_0F1+F2 and M_0F1+F2+F3) or as dual- or triple-side fillers (M_0F1/F2 and M_0F1/F2/F3). As will be explained in the following section of migration (Section 4), the use of dual- or triple-side fillers are associated to the advantage of limiting the migration of the M_0F, which will be connected to the toxicity of the PM_0C (Section 5).

4. Migration

The migration is of great importance in the risk assessment regarding the toxicity and the environmental impact of the PM_0C. Thus, a

meticulous understanding regarding the behaviour of particle migration is essential. The evaluation of the migration usually involves the immersion of the composite film in a food simulant (*i.e.*, a liquid media that mimics the behaviour of actual food) under defined conditions of temperature and time, according to the guidelines of each regulatory agency (EC, 2011).

Most literature on PM_0C used in food packaging perform these migration tests, having generally as the reference threshold values the ones stablished by the European Union in the Commission Regulation No. 10/2011 (EC, 2011). This regulation establishes overall migration limits (of all substances inside the film) of 10 mg of total substance released per dm^2 of food contact surface (mg/dm^2), equivalent to 60 mg per kg of food. Moreover, specific migration limits (one substance inside the film) are also established in mg of substance per kg of food simulant, having as examples the specific limit of 5 mg/kg for copper, 48 mg/kg for iron, and many others. For substances not authorized to be used in food contact materials, according to the list presented in the regulation, the limit of 0.01 mg/kg is applied. Therefore, investigations on the development of novel polymer-metallic packaging films usually aim to fulfil these migration limits but, at the same time, to achieve the desirable active effects.

The migration behaviour, taking binary-PM_0C as the model, has been thoroughly investigated by several authors. They reached a consensus that the migration in contact with a liquid environment, such as in the case of a food simulant and consequently a food sample, can be resulted from several mechanisms or combinations of these. These mechanisms include: (i) *diffusion* of the particulate form from the interior of the film to the foodstuff; (ii) *desorption* of the particulate form at the polymer-foodstuff interface (*i.e.*, in the surface of the film); and/or (ii) *dissolution*, in which, surface or internally located particles dissolve into ions (*i.e.,* metallic ions) and diffuse to the foodstuff (Duncan & Pillai, 2015). Release caused by (iv) polymer matrix degradation due to mechanical or chemical destructive effects, is also referenced as another migration mechanism, however mostly applied to prolonged used applications (*e.g.,* in construction, vehicles, etc.) (Duncan & Pillai, 2015).

Metallic ionic form migration. Given the migration results of several studies, some deliberations can be made regarding the migration behaviour of PM_0C when in contact with food simulants and real food samples. The migration in the ionic form usually follows a general trend, in which, an increase is observed with increased loading content, immersion time, temperature and pH acidity of the food simulant or real food sample. For instance, Liu et al. (Liu, Hu, Zhao, Shi, & Zhong, 2016) in a CuNPs-LDPE binary film (50 nm) observed an increased migration rate with increased temperature (max. at 70 °C), loading content (max. at 0.25 wt%), and pH acidity of the food simulant (max. in 3% acetic acid). Moreover, the same authors tested the food samples of rice vinegar, bottled water and Chinese liquor, reaching a maximum release of 540 μg/L in the rice vinegar (the most acidic food sample).

Metak et al. (Metak, Nabhani, & Connolly, 2015) tested the migration of a AgNPs-PE binary container and surface coated film in various food samples (orange juice, apple, cheese, ground beef, butter, bread, milk powder, carrot and water), reaching a maximum of 5.66 μg/L for the container and 28.92 μg/L for the surface coated film both in the orange juice, which is the most acidic of the used food samples. Other metallic ion migration results can support these deliberations and are presented in Table 1 (Cao et al., 2018; Jiang, Yu, Li, Zhu, & Hu, 2019; Lomate et al., 2018).

The M_0F characteristics in terms of size and composition have also influence on the ionic migration rates, in which smaller sizes have the tendency to migrate at a higher rate, as demonstrated by Weiner et al. (Weiner, Sharma, Xu, Gray, & Duncan, 2018) in AgNPs-LDPE binary films filled with AgNPs of multiple sizes (4, 10, 17, 23, 31, and 41 nm). The authors observed that in 3% acetic acid a maximum migration rate (*i.e.*, the migration value giving the total metal in the AgNPs-LDPE film) of 52% for the 4 nm AgNPs was detected, in contrast with only 0.17% for 41 nm AgNPs.

The same authors also observed that particle composition influenced the migration rates when using AgNPs, Ag_2SNPs (silver sulphide) and AuNPs as fillers (Weiner et al., 2018). Small release quantities of Ag^+ (0.002% in acetic acid) and $Au^{+/3+}$ (0.12% in water) were detected for the Ag_2SNPs (11 nm) and AuNPs (3.2 nm), respectively, in comparison to the high release of Ag^+ for AgNPs with similar particle sizes of 10 nm (0.56% in acetic acid) and 4 nm (41.08% in water). Particle stability was pointed out as the main reason for this behaviour, and related to the dissociation energies of 216.7 kJ/mol for Ag–S (Ag_2SNPs), 226 kJ/mol for Au–Au (AuNPs), and 162.9 kJ/mol for Ag–Ag (AgNPs), with the AgNPs being more easily oxidized and less stable.

The polymer properties must also be accountable, in which the crystallinity degree, water uptake or O_2/H_2O gas permeability can play a big role in the migration behaviour. For example, Palza et al. (Palza, Quijada, & Delgado, 2015) in several CuNPs binary films (Table 1), demonstrated that the ion release occurred in the following order: PA6 > PPC18 > PP > HDPE. The higher release from PA6 and PPC18 was related to their high hydrophilic nature (water diffusion) and low crystallinity (20–25%) in comparison to the non-polar and high crystalline (43–65%) HDPE and PP polymers. Thus, the use of hydrophilic polymers with high levels of water uptake or O_2/H_2O gas permeability are susceptible polymer matrices to high ionic migration levels.

This is often observed in biodegradable films known for their high-water uptake, increased swelling and poor O_2/H_2O gas permeability. For instance, Cano et al. (Table 1) (Cano et al., 2016) in a AgNPs-Starch/PVA binary film, revealed migration rates of 100% of the total silver incorporated in the biodegradable film within a few hours. As causes, the high hydrophilic nature and consequent high-water uptake and swelling, favoured the high migration rates observed.

In all the reported literature here presented (Tables 1 and 2) the ionic form is regarded as the migrated form of the M_0F, and thus the *dissolution* may be suggested as the main migration mechanism in PM_0C due to M_0F oxidation. The release due to oxidation was proved by Weiner et al. (Weiner et al., 2018) that checked that the Ag^+ migration in a AgNPs-LDPE was 5 times lower when samples were stored under anaerobic conditions, meaning that the presence of an atmospheric aerobic condition caused the oxidation of the AgNPs and hence higher migration values.

Metallic particulate form migration. As mentioned before, the determination of the form of the migrated M_0F is critical for a careful risk assessment of the PM_0C to be used in food packaging applications. Although most studies show small to negligible migration values, and thus within the regulatory threshold values, they usually do not differentiate the form in which the M_0F is migrating, whether the ionic form, particulate form, or both. As previously discussed, dissolution (metallic ionic form) is not the only possible migration mechanism, and hence, diffusion and desorption, in which the particulate form of the M_0F migrates, may be present. For example, Mackevica et al. (Mackevica, Olsson, & Hansen, 2016) in commercial packaging products containing Ag particles, detected both the presence of the ionic and the particulate (10–100 nm) form of Ag in all food simulants (3% acetic acid, water and 10% EtOH) with the use of TEM (transmission electron microscopy) analysis, and concluded a general trend of the ionic Ag being higher in the 3% acetic acid, and the particulate Ag higher in water and 10% EtOH.

In another study, Artiaga et al. (Artiaga, Ramos, Ramos, Cámara, & Gómez-Gómez, 2015) using a commercial food package containing AgNPs, detected particulate AgNPs (40–60 nm) in both 3% acetic acid and water simulants by using the AF^4-ICP-MS (asymmetric flow field flow fractionation coupled inductively coupled plasma-mass spectrometry) technique. Furthermore, Metak et al. (Metak et al., 2015) tested the migration of commercial PE films surface coated with AgNPs with real food samples, and detected particulate Ag with sizes between 100-300 nm and 5–10 nm in a milk powder and orange juice sample, respectively, using SEM (scanning electron microscopy) and TEM analysis.

Solutions to hinder migration. As migration is directly related to

the safety regarding the use of PM_0C as food packaging, solutions to hinder the migration (especially of the particulate form) could help achieve a control over the release, and hence assured safety. Pointing off some examples, for instance, the use of ternary or quaternary composite films, in which the M_0F is added separately or physically/chemically immobilized (*i.e.*, dual- or triple-side fillers) with other inorganic fillers, may have potential to hamper the release of the M_0F. This is mostly due to (i) a synergistic improvement of the polymer properties related to migration (*e.g.*, water uptake, O_2/H_2O gas permeability or crystallinity), and (ii) due to the fact that the M_0F, in the case of the dual- and triple-side fillers, is physically/chemically immobilized, which in turn can delay the release of the metallic ions (since the oxidation of the M_0F is obstructed) and inhibit the migration in the particulate form.

Various examples are discussed in Table 2, where we can see that the migration levels detected in ternary or quaternary composite films are usually low (Biswas et al., 2019; Tiimob et al., 2017; Vishnuvarthanan & Rajeswari, 2019; Wang et al., 2020). A good example on how the use of a dual-side filler can hinder the migration of the M_0F, is described in the study by Wu et al. (Wu et al., 2018) in which the incorporation of an AgNPs/Laponite dual-side filler into a chitosan film allowed a decrease in the migration rate (4.4–4.6%) in comparison to the AgNPs-chitosan film (26.5–29.1%), and this was related to the improved water uptake and O_2 gas permeability in the AgNPs/Laponite-chitosan binary film.

5. Regulation aspects and human toxicity impact

Regulations regarding to the specific use of M_0F (*i.e.*, zero valent metallic micro-/nanoparticles) added alone (binary) or in complementation with other fillers (ternary and quaternary) as food contact substances/materials (FCS) is relatively poor. Indeed, by performing a thorough search in both FDA (United States Food and Drug Administration) and EFSA (European Food Safety Authority) databases, a dual-side filler named silver-silica, consisting of a microscale material with the AgNPs coated within the ceramic matrix (silica), is found approved by the FDA to provide antimicrobial action (FDA, 2020). Other related materials to impart antimicrobial action as FCS can be highlighted, such as silver-containing glass, silver-sodium-hydrogen-zirconium-phosphate, silver chloride coated onto titanium dioxide, or modified zeolites with ionic silver, copper and/or zinc. However, in these substances, the metal is added in the form of a metallic ion and not as a M_0F (EC, 2020a, 2020b; FDA, 2020).

The use M_0F as FCS is clearly limited, and most of the approved inorganic substances in the nanoform fall within the category of metal oxides (such as titanium nitride, silica, iron oxide, titanium oxide surface-treated with fluoride-modified alumina, zinc oxide, etc.), carbon black and clays, subjected to certain size restrictions (Garcia et al., 2018; He et al., 2019). Interestingly, the EU regulation on food additives classifies silver (Ag, E174), gold (Au, E175), and aluminium (Al, E173) in their elemental form as approved food additives (EC, 2020a, 2020b). The EFSA has re-evaluated silver (E174) and gold (E175) as food additives, and concluded that the available information concerning the toxicity was insufficient to perform a risk assessment, and recommendations regarding the inclusion of the mean particle size and distribution present in the powder form, is recommended (EFSA, 2016a; 2016b).

Despite the lack of approval in the use of M_0F as FCS, the agencies are fully aware of the spread in the development of PM_0C films with the intention to be applied in food packaging. To this aim, both FDA and EFSA have release several guidance's for industry to fully evaluate the use of nanomaterials in food ingredients and food contact substances (Garcia et al., 2018). The EFSA, for example, has released a document that provides guidance on risk and safety assessment on the application of nanoscience and nanotechnologies in the food and feed chain, to assist the industry in assuring the safety of their products (Hardy et al., 2018).

This document provides guidance on (i) the correct definition of a nanomaterial (≥50% of the particle size distribution must be in the size range of 1–100 nm); (ii) the necessary information regarding the nanomaterial characterization to properly assess the material safety; and (iii) the steps regarding the testing of the toxicological profile of nanomaterials. A highlighted expression used in this guidance, and important to assess the safety of a nanomaterial, is the "stability parameter" that is related to the point in which the nanomaterial losses its nano specific properties (*i.e.,* "transformed" to a non-nanosized material), happening due to high degradation rates under certain environments (*e.g.*, dissolution in water), or the formation of larger aggregates of sizes superior than 100 nm.

These guidance's reflect the importance of treating a nano-based product as a "case-by-case" or "product-by-product" analysis to assess the risk of the nanomaterial, since due to the enormous physicochemical differences that nanosized materials have in contrast to its corresponding elemental and bulk (not in nanoscale) form, conventional safety procedures and regulations cannot be applied to their nanosized form (Garcia et al., 2018; Hardy et al., 2018). In relation to the human health impact by the use of PM_0C films as food packaging, the migration of the M_0F (especially in the particulate form; however high levels of ionic metals are also problematic) into the foodstuffs could lead to their ingestion, having as the major unsettling matter, when the particulate form migrates into the foodstuff.

As an example of a safety evaluation by the EFSA of an iron/bentonite (8–20 μm size) dual-side filler fabricated by NanoBioMatters Industries (Spain) to be applied as food contact material, concluded that the material dues not raise a safety concern for consumers with a maximum loading of 15% w/w, giving the migration levels of iron (4.5 mg/kg) and aluminium (0.3 mg/kg) being smaller than the regulated threshold values for iron (48 mg/kg) and aluminium (0.8 mg/kg) (EFSA, 2012). However, it is important to mention that despite the safety report did not indicate the presence of nanomaterial, in a paper of the same year of an iron/kaolinite, also manufactured by NanoBioMatters Industries (Spain), an iron average particle size of 115 nm with a distribution of 75–220 nm immobilized within the kaolinite was detected, thus confirming the presence of nanomaterials (Busolo & Lagaron, 2012). This dual-side filler was melt-blended with HDPE and LLDPE for oxygen scavenging purposes, and the authors showed negligent iron and aluminium migration values in water and isooctane as compared to standard threshold values. However, the evaluation of the presence of migrated iron particles was not performed and should be an additional safety measure to be implemented. Certain authors did evaluate the toxicological impact of PM_0C films as presented in Table 3.

Based on these studies, the cytotoxicity is clearly related to the migration capability of the M_0F amount in both the ionic and the particulate form, in which thermoplastic based metallic composite films demonstrated lower cytotoxicity effects (Jiang et al., 2019; Oliani et al., 2017) in comparison to biodegradable based polymer matrices (Basak et al., 2018; Wu et al., 2018). This was related to the migration differences between both polymeric matrices (as discussed in section 4). For instance, in a study by Palza et al. (Palza, Galarce, Bejarano, Beltran, & Caviedes, 2017), the authors stated that the highest toxicity for the CuNPs-alginate (Table 3) was due to both the migration of the ionic and particulate inorganic form, in contrast to the only ionic form migration in the PP-CuNPs film. When the M_0F is added in the form of a dual-side filler, the cytotoxicity effect decreased in comparison to the sole addition of the M_0F (as binary film). This fact was related to metallic migration constrains (Sarwar, Niazi, Jahan, Ahmad, & Hussain, 2018; Wu et al., 2018), as discussed in Section 4. The lack of more profound investigations regarding the toxicity of M_0F inside a polymeric matrix is evident, and based on these results, a careful inspection of the migration is strictly necessary in order to fully evaluate the toxicity impact of such materials.

6. Environmental impact

Another aspect of great importance is the environmental impact that the implementation of polymer-metallic composite films may cause.

Table 3
Cytotoxicity studies of polymer-metallic composite films.

Polymer-metallic composite film	Procedure[1]	Cytotoxicity	Ref.
AgNPs-Gelatin/PVA (SC film)	MTT assay; PBMC cell line	Cell viability of the film (0.1 mM Ag) was ~84.14%; Classified as light poisonous (75–99% cell viability)	Basak et al. (2018)
CuNPs-PP (MB film)	MTT assay; L02 cell line	Cells treated with Cu^{2+} with varied concentrations (0–80.0 μg/g); Significant inhibition on cell viability was observed starting from the 10.0 (70% cell viability) to 80.0 (20% cell viability) μg/g concentrations; Giving the maximum migration of 4.5 μg/g from the CuNPs-PP (1.0 wt%), the film was considered safe to use	Jiang et al. (2019)
AgNPs-PP (MB film)	ISO 10993-5:2009; NCTC L929 cell line	Film samples (0.1–4.0 wt% of AgNPs) were characterized as noncytotoxic (above 50% cell viability)	Oliani et al. (2017)
CuNPs-PP (MB film); CuNPs-Alginate (SC film)	MTT assay; CNh and SaOS-2 cell line	CuNPs-alginate (0.5–5.0 wt % CuNPs) presented <40% viability in both cell lines vs alginate control (~40% viability); CuNPs-PP films (10, 20 wt% CuNPs) presented 60–70% viability vs control PP (60–70%) in CNh cells, and 50–60% viability vs. control PP (50–60%) in SaOS-2 cells	Palza et al. (2017)
AgNPs+NC-PVA (SC film)	MTT assay; HepG2 cell line	Non-toxic effect for AgNPs (1.0, 3.0 wt%) + NC (12 wt %)-PVA films at the concentrations of 35–250 μg/mL by obtaining a cell viability higher than 90%	Sarwar et al. (2018)
AgNPs/Laponite-Chitosan (SC film)	MTT assay; L02 cell line	Cell viability of AgNPs/Laponite-Chitosan, pure Chitosan, and AgNPs-Chitosan were 85.81, 90.37, and 41.51%, respectively, using 10 mg film samples	Wu et al. (2018)

([1]) MTT (3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyltetrazolium bromide assay); PBMC (primary peripheral blood mononuclear human cells); L02 (human normal hepatocyte cell line); ISO10993-5:2009 (biological evaluation of medical devices part 5: tests for in vitro cytotoxicity); NCTC L929 (mouse fibroblast cell line); CNh (cerebral cortex of normal fetal mice cell line); SAOS-2 (human osteosarcoma cell line); HepG2 (human hepatocellular carcinoma cell line).

Even if the fabricated composites are effective as active food package and comply with the migration regulation limits, the question regarding the effects that can cause in the environment has been raising concern among the scientific community. Are the benefits of using PM_0C food packaging materials outweighed by the possible environmental burden? Indeed, very few investigations study the real effect of these materials in the environment. In the last couple of years, an increase amount of studies has been focused on the use of life cycle assessment (LCA) as a systematic tool for determining the environmental impact of metal-based food packaging products by considering the different stages of the product lifetime, such as the raw materials used in the composite film manufacture, the manufacturing process, usage time, and end of life or disposal (Westerband & Hicks, 2018a).

In an LCA study, the environmental impact of hypothetical PE containers filled with AgNPs containing a high (766 μg) or low (65 μg) load was evaluated (Westerband & Hicks, 2018a). The study resulted in an insignificant increase (less than 2%) of the overall environmental impact in the ecotoxicity, carcinogens, non-carcinogens, eutrophication and ozone depletion, compared to conventional packages. As conclusion, the impact in the addition and leaching of AgNPs is minimal *vs.* the advantages in reducing food waste, making it a viable option to use as food packaging materials. The same authors, (Westerband & Hicks, 2018b) used LCA to evaluate the environmental impacts of the same hypothetical AgNPs-PE containers in the storage of food samples (chicken, bread and orange juice). In the categories of global warming (0–64% reduction) and acidification (~12% reduction for chicken and ~1200% reduction for orange juice), the use of AgNPs-PE allowed a decrease in those categories in function of the extended lifetime, suggesting the environmental benefit of using AgNPs enable food containers. However, in the category of ozone depletion, an increase in the environmental impact was observed. Thus, in conclusion, the authors stated that the potential environmental benefit is highly dependent on the environmental impact of the stored food.

Pourzahedi et al. (Pourzahedi, Vance, & Eckelman, 2017) performed an LCA study for 15 commercially available AgNPs-filled products. The environmental impact strongly depended on the silver loading (superior than 10%) and type of product, affecting all environmental categories (ozone depletion, global warming, photochemical smog, acidification, eutrophication, human heath: carcinogens, human health: non-carcinogens; human heath: criteria air pollutants, ecotoxicity and fossil fuel depletion) with increases between 1 and 99%. Moreover, the metal precursors, heating requirements, and electricity consumption in the AgNPs synthesis method, strongly influenced the environmental impact with increases as high as 300% in eutrophication, carcinogenic, non-carcinogenic and ecotoxicity impact, 100% for acidification, 230% for smog, and 20% for ozone depletion, global warming and fossil fuel depletion. This was done by comparing physical (*e.g.*, flame spray pyrolysis), chemical (with sodium borohydride or trisodium citrate) and bio-based synthesis methods, with the physical method having the greatest impact level. The authors also evaluated the ecotoxicity effect of the migrated Ag from the products, and by considering the product with the highest migration, the food container (7.95 mg Ag; 2% release), the authors concluded that it has 2–12 times less ecotoxicity than the food container itself, considering all possible transformations and processes that can happen on the released Ag occurring during waste water treatment, such as sulfidation reaction, dissociation into ions, etc.

In another investigation, Bi et al. (Bi et al., 2018) evaluated by LCA the environmental impact of a commercial antimicrobial container of PP containing silver (8.8 ± 0.6 Ag μg/g of polymer; >300 nm particle size) considering three different lifecycle phases: raw manufacture of the container, silver release during dishwashing and during landfill disposal. After the dishwashing experiment at 60 °C, the total Ag released was of 23 ng/g (0.25%) with detergent and 13 ng/g (0.13%) with only water, suggesting the detergent role in promoting migration. Detectable Ag sizes in the dishwashing extracts by using sp-ICP-MS were of 40 nm to more than 100 nm when using detergent, and 40–90 nm using only water, and interestingly, the size of the detected particles decreased with increasing washing cycles (4 in total). Landfill silver release was evaluated by a toxicity characteristic leaching protocol (TCLP) to evaluate the hazardousness of a waste, where less than 1 μg/L during a 18 h test was detected, which is lower than the 5 mg/L threshold value to be considered toxic in disposal. Regarding the environmental impact, increases in all environmental impact categories are detected and vary between 0.05 and 1.4%, with the highest impacts in ozone depletion (0.81%), carcinogenic (1.38%), noncarcinogenic (0.80%) and ecotoxicity (<0.2%). Moreover, the authors performed an antibacterial test against *E. coli*, and found insignificant effects in the reduction of the bacterial count. In conclusion, the additional environmental burden (although being very small) in comparison to the potential health risks associated to nanoparticle migration and the fact that no antibacterial activity was detected, the incorporation of silver was considered unnecessary.

Based on the mentioned literature, the environmental impacts of PM_0C can vary in terms of the filler loading degree, type of synthesis

methods to manufacture the M_0F, and the initial environmental impact of the food to be stored. The toxicity and environmental impact are also strictly related to the migration capability of the ionic or particulate form, and hence, strict regulations must be implemented in the migration evaluation. Indeed, this is all for nothing if the addition of the M_0F does not perform its activity. It is very important to double-check if the active property is present, prior to their market entry, so that no unnecessary environmental burden and human toxicity related problems are generated (Bi et al., 2018).

7. Conclusions

Polymer-metallic composite films exhibit promising potential to be used in the food packaging industry. Antimicrobial activity, scavenging abilities, or antioxidant effects are some of the active properties that the metallic particles can add to a polymeric film. In consequence, their application as food packaging options (*i.e.*, as containers, bags, etc.) have a positive effect on the extension of food shelf life, safety and quality, and hence, diminishing food waste.

Despite the advantages, special care must be taking regarding the migration behaviour of such fillers, especially in the particulate released form, since it is directly connected to an increased toxicity and environmental impact. A proper characterization with more sensitive analytical techniques of the migration extracts is a necessity, in order to effectively detect the type of migration form (particulate or ionic) of the metallic filler. This will aid in understanding the stability of the metallic fillers outside of the polymeric matrix, in terms of dissolution, aggregation, or other physicochemical changes, which is an important parameter to evaluate the risk level of the composite film.

The development of this type of composite films is advancing in an enormous rate, and the regulation regarding the use of metallic micro-/nanoparticles in food contact materials, needs to be in the same pace. Proper risk assessments regarding human toxicity (*e.g.* by stablishing certain migration acceptable levels for human safety) and the effective evaluation and confirmation of the advantages on the use of metallic particles is needed, so that the regulation and legislation can advance into the approval of this type of materials for food contact packaging. Research in the development of strategies to mitigate and control the release of the metallic filler may pose as an interesting field so that the negative consequences in terms of toxicity and environmental impact can be minimal.

Author contributions

Diogo Videira-Quintela: conceptualization; investigation; methodology; roles/writing – original draft; writing – review & editing; **Olga Martin**: conceptualization; methodology; visualization; writing – review & editing; supervision; **Gemma Montalvo**: conceptualization; methodology; visualization; writing – review & editing; supervision.

Declaration of competing interest

None.

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