Recent Advances and Migration Issues in Biodegradable Polymers from Renewable Sources for Food Packaging

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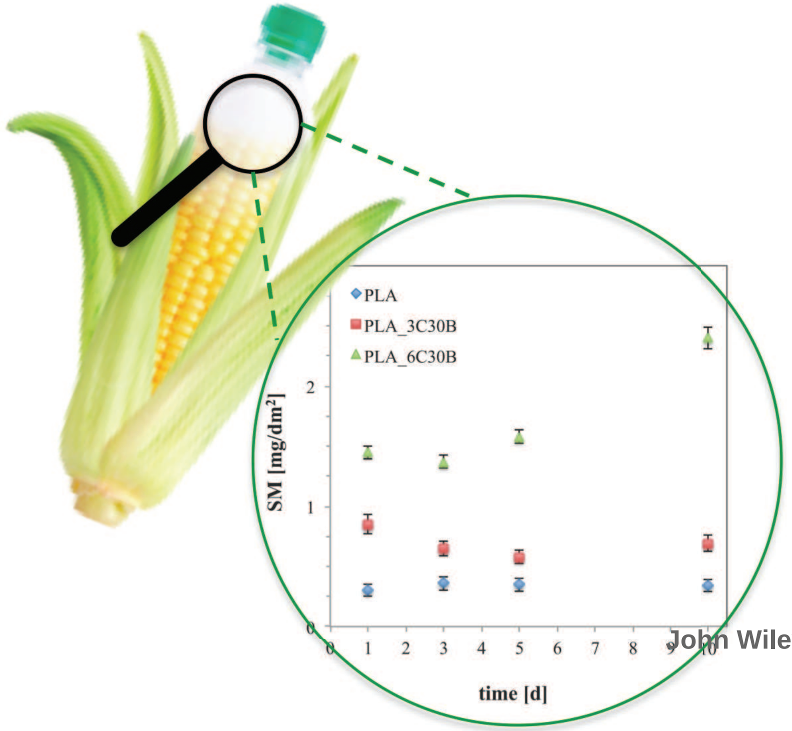
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TITLE OF MANUSCRIPT

Recent Advances and Migration Issues in Biodegradable Polymers from Renewable Sources for Food Packaging

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ABSTRACT

In recent years, consumers demand for environmental sustainability and legislative actions are pushing the plastic packaging industry towards bio-based plastics. However, despite the advantages related to their ecofriendly nature, the commercial large-scale applications of the bio-based polymers to substitute the conventional ones as packaging materials are till now limited, because they show some limitations in their processability and lower performances, specially in terms of diffusion barrier properties to small molecules, which have a critical role for food contact uses. Main strategies used to overcome these issues involve the blending with other biopolymers and/or the addition of other substances such as micro- and nanofillers and plasticizers. This review reports on most recent advances and upcoming possibilities in food packaging applications having potential commercial interest of selected biodegradable polymers from renewable sources, focusing the attention on the issues related to the food/packaging interactions and the possible consequent migration of substances.

KEYWORDS

Biodegradable and renewable polymers; food packaging; migration; nano-biocomposites; blends; barrier properties.

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INTRODUCTION

In last decades, the growing consumer sensitivity towards environmental concerns, and the increasing demand for renewable and bio-based materials, supported also by legislative actions on environmental protection, sustainability and waste management, are driving the market towards the development of eco-friendly, biodegradable plastics. The packaging field contributes now over 50% of the global biodegradable plastics consumption and, according to a recent study by Smithers Pira, the demand for bioplastics in packaging is expected to rise at an estimated Compound Annual Growth Rate (CAGR) of 33%, in the period 2013-2023, as the materials become cheaper and improvements in properties lead to a wider variety of possible applications.[1] This trend is driving the research towards the development of new and increasingly performing biodegradable systems, also through modifications approaches, as well documented by the wide scientific literature available.

Biodegradable polymers can be classified according to the source of their origin, i.e. renewable or petrochemical, or according to the method of their production, giving the following main categories:

- Polymers produced by direct extraction from biomass, e.g. polysaccharides as cellulose, pectin starch and chitosan, and proteins as gelatin, casein, soy protein, zein, and wheat gluten.
- Polymers obtained from microorganisms or genetically-modified bacteria, e.g. polyhydroxyalkanoates (PHAs), bacterial cellulose, xanthan, and pullulan.
- Polymers produced by conventional chemical synthesis from renewable or non-renewable monomer feedstock, e.g. polylactic acid (PLA), poly(ε-caprolactone) (PCL), poly(butylene succinate) (PBS), and poly(vinyl alcohol) (PVA).
- Polymers produced by blending, e.g. starch-polycaprolactone blends and starch-cellulose derivatives.

Among the currently available bioplastics, PLA, starch and PHAs are the most interesting from a commercial point of view because they can be processed with conventional converting equipment, have a satisfactory balance of functional properties and are produced on a large industrial scale at competitive prices.

PLA is a thermoplastic polymer that belongs to the family of aliphatic polyesters, degradable by simple hydrolysis of the ester bond. Polymerizing a controlled mixture of the two optical L- or D-isomeric forms of the lactide monomer (in terms of ratio and sequence of arrangements), its stereochemical structure can be easily modified, in order to yield a wide spectrum of high-molecular-weight polymers, amorphous or crystalline, having tuned properties.[2-6] PLA with PLLA content higher than 90% tends to be crystalline, with melting temperature (Tm) and glass transition temperature (Tg) increasing with the optical purity.[7-10] High-molecular-weight PLA, certified as Generally Recognized as Safe (GRAS) by the US FDA, is a odorless, colorless, glossy, stiff, biocompatible, low toxic polymer, suitable for food contact applications, with properties similar to polystyrene.[11] The major use of PLA is in food packaging applications, as well as in the pharmaceutical and biomedical fields.[12-13] In particular, thanks to its desirable properties such as flavor, aroma and grease resistance, high clarity and printability, PLA offers great potential for short-lifespan packaged foods, such as yoghurts and fruit and vegetables, or for juice and mineral water, and for disposable tableware.

Starch is one of the most abundant natural polysaccharides.[14] The main agricultural sources for starch production include corn starch, wheat, potato, and cassava.[15-16] It is composed by two major components: amylose (linear) and amylopectin (branched), which relative content varies depending on the botanic origin of the starch and on the growing conditions, thus influencing the physicochemical properties of the starch.[17-20] Native starch is not a thermoplastic material, therefore starch films are commonly produced by casting, even if starch can also be processed by extrusion technologies after thermoplasticization.[20-24]

Polyhydroxyalkanoates (PHA) are polyesters of various hydroxyalkanoates that are naturally synthesized by many bacteria, generally cultivated on agricultural raw materials.[25] Large-scale commercial production of PHAs uses fermentation technologies. The PHAs are non-toxic and biocompatible, have good ultra-violet resistance and physical chemical properties considerably dependent on the monomer composition.[26-29] The main member of the PHA family is the homopolymer poly(3-hydroxybutyrate) (PHB): it is a semicrystalline, isotactic stereoregular polymer, with a high level of biodegradability and material properties considered similar to polypropylene (PP).

Despite the advantages related to the ecofriendly nature of these polymers, their commercial applications on a large scale to substitute conventional polymers as packaging materials are till now limited, mainly because all of them present some drawbacks in their properties (mechanical, moisture barrier, thermal, dimensional, etc.). The main critical points concern some limitation in their processability and the reduced barrier properties to small molecules such as water and oxygen.[12-13,17-20,30-31] The last point, in particular, can make the biopolymer-based packages little effective in assuring adequate quality, safety and shelf life of the packaged foods preserving them from deteriorative chemical changes (e.g. nonenzymatic browning, hydrolysis and/or oxidation of lipids, proteins, vitamins and oligo- and polysaccharides, degradation of natural pigments, etc.), from changes in their flavor (due to aroma sorption or transfer of undesirable flavors from the packaging to the food), and from the migration of substances from packaging material to the packaged food. Therefore, in order to improve their performance, the blending with other biopolymers, the chemical derivatization or the addition of other substances such as fillers and plasticizers are generally required. All these strategies are currently widely investigated in literature and a number of compositions based on PLA, starch and PHAs have been tested that resulted particularly beneficial on several properties of interest for food packaging applications.[20-21,32-48]

Since there is an abundance of literature dealing with the above biodegradable polymers, in our present paper we will report on most recent developments and upcoming possibilities in food packaging applications of potential commercial interest of selected materials from renewable resources based on PLA, starch and PHAs, focusing the attention on the food/packaging interaction issues and the possible consequent migration of substances.[49-55]

In Europe, biodegradable plastics are regulated in the same manner as conventional plastic materials, under Commission Regulation EC 10/2011, and all the substances used in the manufacturing of biodegradable plastics must be listed on Annex I of the regulation.[56] However, due to differences in physical chemical properties between conventional and biobased materials, which implies that pure bioplastics are usually less stable and have a lower diffusion barrier than conventional plastics, more additives are usually used in biodegradable plastics. Therefore, some undesirable interactions and consequent migration of substances may be more or less relevant for one than for the other. Nevertheless, few studies are reported in literature about the safety assessment of food packaging made of biodegradable polymers.

The most studied biopolymer is PLA. Migrants from PLA may include lactic acid, the linear dimer of lactic acid (lactoyl lactic acid), other oligomers of PLA (n. 3–13), and the cyclic dimer of lactic acid (lactide).[57-58] Among them, lactic acid is included in the list of authorized monomers and other starting substances in the European Directive EC 10/2011 with no restrictions or specifications. LA or PLA oligomers are not included. Similarly, in the United States, according to e-CFR 184.1061, lactic acid is affirmed as a GRAS food ingredient and no comments related to LA or PLA oligomers are included.[59]

Migration from pure PLA is reported to be low.[57-58,60-61] Mutsuga et al. in 2008 performed lactic acid, lactide and oligomers migration tests on several types of PLA sheet in water, 4% acetic acid and 20% ethanol, using short and long contact times and different temperatures, ranging from 20°C to 95°C. Lactic acid migration after short-term tests (60°C, 30 min) was detected at levels of 0.08–0.40 $\mu g/cm^2$ from all the samples, into water, 4% acetic acid and 20% ethanol. The migration values increased under acidic or high-temperature conditions. The same tendency was also found for the migration levels of lactide and oligomers. Moreover, the authors demonstrated that PLA remained stable over 6 months at 40°C, whereas started to decompose at temperatures above Tg, so that the migrant levels increased, particularly for PLA that contained high D-lactic acid levels.

In the case of food packaging PLA formulations incorporating plasticizers, stabilizers, nanofiller and other biopolymers able to improve the properties of the final article, a potential modification of the migrational behavior of the PLA may occur. All these compounds, in fact, have low Mw with a potential to diffuse through the polymeric matrix when used in packaging or articles in contact with food.[62] Therefore, more studies are needed for its blends and copolymers, and also for all the compounds that are applied or added for improving physical, mechanical, and barrier properties of PLA.

Di Maio et al. have recently developed nanocomposite PLA films added with Cloisite 30B clay-derived nanofiller having one nanometric dimension, and have characterized the obtained systems in terms of functional properties and total and lactic acid specific migration, in view of food packaging applications.[63] The films were produced using a laboratory-scale film production pilot plant, demonstrating that conventional film production technologies are adequate to disperse the layered nanofillers in the PLA matrix on a nano-scale with intercalated/exfoliated morphology. With respect to the unfilled PLA, the developed nanocomposite systems show a marked improvement of the mechanical performance, with a rise in the modulus and in the elongation at break, and a significant lowering in the oxygen permeability that decreases up to ca. 61% for the film added with 6wt% of nanoclay. In view of food packaging applications, the authors have also verified that the migration behaviour of the nanocomposite PLA accomplishes the safety requirements set down by the legislation for the food contact plastics, accordingly to the most recent European Union legislation (EC 10/2011) that authorizes on a case-by-case basis the use of engineered nanosized particles as additives for food packaging materials.[56] With this aim, total and lactic acid specific migration tests were performed using the aqueous-based simulants, selected as worst case for potential migration from PLA (Tables 1-2). In particular, 3% acetic acid, simulant for acidic character of foods, and 50% ethanol, simulant for migration in milk and dairy foods, were considered. The obtained results demonstrated that the nanoclay incorporation into PLA films does not change detectably their overall migration, which is in the range 0.5-0.8 mg/dm^2, in compliance with the migration limits (10 mg/dm^2) as set down by the EU legislation for the food contact plastics (Table 1). Similarly, the nanofiller does not affect the lactic acid specific migration in 3% acetic acid that remained always at no significant levels (Table 2). On the other hand, the lactic acid migration in 50% ethanol increases along with the nanofiller amount in the film samples, while remaining well below the applicable specific migration limit, according to the migration results plotted in Figure 1. The higher swelling capability of the 50% ethanol towards PLA compared with the 3% acetic acid is responsible of the higher specific migration levels of lactic acid in the alcoholic simulant.

Fortunati et al. investigated the effect of pure and modified cellulose nanocrystals (CNC) on the properties of PLA nano-biocomposites produced by solvent casting, focusing the attention on the changes in gas transport and overall migration behavior.[64] They found that both unmodified and modified CNC had a positive influence on the barrier properties of the nano-biocomposites, which improved as a consequence of the higher tortuosity of the the penetrant molecules pathway across the PLA matrix, induced by the nanofiller addition. The effects are more relevant when modified CNC was used, due to a better interaction of the nanofillers with the polymer matrix. In particular, respect to pure PLA films, the systems added with 5% of modified CNC gave the highest reduction in oxygen transmission rate (OTR) of ca. 48%, whereas those added with 1% of modified CNC showed the highest reduction in water vapor permeability (WVP) of ca. 34%. In terms of migrational behavior, overall migration tests, performed according to Commission Regulation 10/2011 using ethanol 10% v/v (simulant A) and isooctane (alternative simulant to D2) as liquid food simulants, demonstrated that PLA maintained negligible migration level even in the presence of both unmodified and modified CNC (Figure 2).

Pure PLA and PLA systems added with CNC at 1% show higher migration levels in ethanol 10% than in isooctane, because the alcohol swells the polymer and then promotes the migration. However, in PLA systems added with CNC at 5% the plasticizing action of the alcohol in presence of the cellulose nanocrystals promotes structural rearrangements of the polymer chains during the incubation in ethanol, so affecting the migration process. As a consequence, these systems show higher migration levels in isooctane than in ethanol 10%. Again, at fixed CNC loading, the overall migration is lower in presence of modified CNC due to a better polymer-filler interaction. The maximum overall migration was 0.16 mg/kg for the systems added with 5% of unmodified CNC in isooctane. Anyway this value is well below the applicable generic migration limit of 60 mg/kg food of the Regulation EU 10/2011.

In a subsequent paper, Fortunati et al. analyzed the effect of the CNC in combination with Ag nanoparticles on the barrier and migration properties of PLA nano-biocomposites produced by solvent casting, intended to be used as active food packaging.[65] The authors demonstrated that the addition of the Ag nanoparticles in combination with modified CNC produced a more efficient barrier to transport of oxygen and water vapor, compared to binary PLA/CNC systems. No samples exceeded the overall migration limits in ethanol 10% and isooctane, even if the migration levels are a little higher in the ternary blends than in the binary formulations without Ag nanoparticles. Specific migration of nanosilver in both simulants was also evaluated in order to ascertain compliancy with specific migration limit of 0.05 mg of silver per kg of food currently referenced by the EFSA.[66] The amount of silver released from different formulations was well below the specific migration limit indicated by the EFSA when the simulant was isooctane, whereas exceeded the permitted limits when the simulant was ethanol 10% (v/v), as a consequence of the plasticization of the PLA matrix in the ethanolic simulant that improves the migration of Ag.

Girdthep et al. developed biodegradable nanocomposite blown films based on compatibilized poly(lactic acid)-poly(-butylene adipate-co-terephthalate) (PLA/PBT) and silver-loaded kaolinite (AgKT) for use as model package for dried fruits.[67] They found that, in systems compatibilized with tetrabutyl titanate (TBT), AgKT enhances gas barrier properties of the films with respect to the neat PLA/PBT polymer blend, giving a reduction of ca. 50% of both water vapor and oxygen peremeability. Moreover, they measured Ag particle migration in slightly acidified water solutions containing acetic acid 4wt%, chosen as simulant solution according to EFSA (EFSA 2004, 2005, 2006 and 2007) and Thai Industrial Standards (TIS 1027-2553), and found that AgKT inhibits bacterial growth on polymer film by function of Ag nanoparticles and allows controlling Ag release for long-lasting antibacterial effect, so saving the product quality. In particular, as shown in Figure 3, compatibilized PLA/PBAT/TBT/AgKT nanocomposite films show a rapid initial releasing rate of Ag ions (0.0036 $mg\cdot kg^{-1}\cdot day^{-1}$ within the first 5 days), controlled only by diffusion, followed by a decreased release rate (0.0021 $mg\cdot kg^{-1}\cdot day^{-1}$ during day 5-14), potentially related to both Ag ion diffusion though the matrix and tortuous paths of KT layers hindering the ion migration. The concentration of released Ag ions at day 14 onwards remains stable at ~0.0348 mg/kg. Such Ag migration complies with the limits as determined by EFSA and TIS standards (0.05 mg/kg and 100 mg/kg, respectively) for plastic bag in contact with food. Accordingly, the developed nanocomposite film can be used safely as an Ag-based package in contact with food.

Mattioli et al. proposed the use of a deposition technology to improve the barrier properties of PLA films and analyzed the gas barrier and overall migraton of PLA films coated with hydrogenated amorphous carbon layers (a-C:H) deposited using a radiofrequency plasma deposition method (rf-PECVD) with different exposure times (5, 20, and 40 min).[68] The authors observed a significant reduction of OTR and WVP values for all PLA/a-C:H films with respect to untreated PLA. In particular, they obtained a reduction in OTR values of ca. 59% and a reduction in WVP values of ca. 68% in the case of PLA/a-C:H treated for 5 min, while a lower effect in the barrier properties to water was detected for the layers deposited with a higher exposure time. The results were explained as a consequence of the presence of more defects and surface cracks in the morphology and carbon crystal structures of the coating layers in these systems, as revealed by FESEM and XPS analyses.

The effect of the a-C:H layers on the migration properties of the coated films were preliminarily evaluated by overall migration tests performed according to current EU legal standards (Commission Regulation EU No. 10/2011), using ethanol 10% (v/v) and isooctane as food simulants. The tests demonstrated that, for all film samples, the migration levels in ethanol 10% (v/v), which plasticize the PLA, was higher than in isooctane, while remaining always well below the limit of 60 mg/kg. Only in the case of PLA/a-C:H treated for 5 min a beneficial effect of the coating layer on the overall migration value in ethanol 10% (v/v) was observed. For the PLA/a-C:H films deposited with longer exposure times the overall migration values strongly increased with the a-C:H thickness, specially in the case of 40 min of a:C–H deposition, where deeper and wider micro-crack were present.

For what concern the starch-based food packaging materials, the main food/packaging interaction issues concern the potential migration of plasticizers and fillers introduced to decrease the melting and processing temperature and to thermo-plasticize the polymer, specially when the food has high affinity (i.e. strong interaction) with the polymer. In fact, even if Avella et al. found that migration of metals from the biodegradable starch/clay nanocomposite films used for packaging of vegetable samples was minimal, several other authors have reported the reduction of packaging performance, with gradual quality deterioration of packaged food, caused by the relevant structural changes due to migration of plasticizers and additives from starch-based films in contact with foods or food simulants.[69]

Zhu et al. analyzed the migration and the associated structural changes of hydrophobic starch acetate films plasticized with triacetinin during contacting with distilled water for different times, demonstrating that the triacetin migration could be described by an overall first-order kinetic model (R^2=0.9324).[70] Similar first-order kinetic model was demonstrated adequate for describing the migration of three natural antimicrobial agents (thymol, carvacol and linalool) into isooctane from starch-based films also by other authors.[71] Zhu et al. analyzed the migration results also by a diffusion model, either at the short-term ($m_t/m_\infty < 0.67$) and the long-term ($m_t/m_\infty > 0.67$), by fitting the release curve ($m_t/m_\infty < 0.67$) to Eq.: $m_t/m_\infty = kt^n$, where k is a constant which characterizes the polymer network system and n is the diffusional exponent characteristic of the release mechanism.[72] The estimated value of n, obtained from the slope of the $\ln(m_t/m_\infty)$ versus ln(t) plot, shown in Figure 4a, was equal to 0.3776 (R^2= 0.9765), which demonstrated that the short-term migration of triacetin can be predominantly described by a Fickian diffusion mechanism (i.e. $n \leq 0.5$) and was scarcely affected by the relaxational phenomena due to the diffusion of solvent and plasticizer within the film matrix. At longer times, the observed sigmoidal shape of the curve (see the inset in Fig. 4(b)) for subsequent migration of triacetin suggested a change of the diffusion model that becomes non-Fickian, because the subsequent migration of triacetin was affected by the structural changes of starch acetate film matrix, revealed by FTIR and SAXD analyses. In particular, the migration of triacetin increased with the increasing penetration of water and then reached a plateau when the starch acetate film matrix was saturated with water. Subsequently, along with the gradual plasticizer migration, the inter-molecular interaction between triacetin and starch acetate was weakened and thus, the inter- and intra-molecular interaction of starch acetate molecules was directly enhanced, giving a more compact aggregation structure within the film matrix.

The same authors in a subsequent paper evaluated the effect of a microwave treatment on the migration of the triacetin plasticizer from the same water-resistant starch-based film into aqueous foods, such as whole milk and skimmed milk, and on the changes in molecular interactions and multi-scale structures (crystalline structure and ordered aggregation structure) of the starch ester film.[73] They demonstrated that the microwave heating accelerates the triacetin migration from the starch ester film to the milk system, compared with the simple immersion at 30°C without microwave. The phenomenon was attributed to the film structural changes, i.e. enlargement of the inter-chain distances in the amorphous region, partial destruction of the crystallite structure and shrinkage of the ordered microregions.

Studies on migration behavior of PHAs at our best knowledge are rare and limited to measurement of overall migration. Bucci et al. in 2007 studied the potential for the use of PHB as packaging for food products and performed overall migration tests in accordance with Resolution 105/99 of the National Environmental Health Agency of Brazil using four different food simulant solvents (distilled water, acetic acid 3%, ethanol 15% and heptane).[74] The authors verified that in all cases the results were below the limit recommended by Resolution 105/99, which is 8.0 mg/dm^2 or 50 mg/kg, and hypothesized that the residue might be monomers released in the PHB production process or additives used in plastics manufacturing processes, such as a white pigment or a mold release agent used in the injection process.[75]

Recently, other researches have been focused on the overall migration of PHB-based nanocomposite films.[76-80]

Díez-Pascual et al. prepared PHB-based bionanocomposites incorporating different contents of ZnO nanoparticles and analyzed their barrier, antibacterial and migration properties.[76] The authors found that the water uptake and the WVP of the nanocomposites decrease with increasing ZnO content, by up to 66% and 38% at 5.0 wt % nanoparticle content, in comparison to the neat biopolymer and related this enhanced behaviour to the higher crystallinity degree and to the more perfect crystalline structure of the PHB/ZnO samples. The same trend was observed in the oxygen permeability values: again, the lowest value was measured for the sample loaded with 5wt% ZnO, probably because nanofillers start to aggregate at higher ZnO contents. The antibacterial activity instead, progressively increased with the nanofillers concentration. In terms of migration, overall migration tests with non-polar (isooctane) and polar (ethanol 10% v/v) simulants demonstrated that the total amount of migrated substances significantly decreased with increasing nanoparticle content up to 5 wt% of ZnO, then remained almost constant (Figure 5). In all cases the overall migration values were well below the legislative limits for food packaging materials.

Yu et al. developed a transparent nanocomposite-based packaging film comprised of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and different concentrations of functionalized cellulose nanocrystals (cellulose nanocrystal methyl ester, CNC-me) and evaluated the barrier and migration properties.[77] The authors observed a noticeable reduction in water uptake and WVP values with increasing the CNC-me concentrations, compared to neat PHBV (Figure 6). The obtained improvements were larger than those reported for ZnO, MWCNT or carbon nano-fiber reinforced PHBV.[78-80]

CONCLUSIONS

This review has discussed the most recent advances and the main research efforts regarding the diffusion barrier improvements, the food/packaging interaction issues and the possible consequent migration of substances of selected bio-based and biodegradable polymers for food packaging applications. In particular, we have looked in the state of the art of PLA, starch and PHAs, which are the most interesting from a commercial point of view and show the most increasing market trend. The reviewed literature is primarily focused on novel formulations based on the addition of other substances such as micro- and nanosized fillers and plasticizers, intended to overcome the limitations of such biopolymers, in terms of processability, stability and structural and functional performance. These formulations are demonstrated effective in improving several properties of technological interest, mainly the diffusion barrier against permeation of low molecules such as water and oxygen, without unacceptable detrimental effect towards migration of undesirable substances from the polymer matrix in most cases. However, most of these studies were only limited to the evaluation of the overall migration and were conducted with food simulant solvents. The testing with real foodstuffs and the knowledge on human health effects and risk assessments are largely insufficient, especially when nanosized additives are contained in the biopolymer formulation, and more research is needed to ensure the safety of this kind of packaging materials in direct food contact applications.

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FIGURE CAPTIONS

FIGURE 1 Specific migration of lactic acid in 50% ethanol from the unfilled and nanocomposite polylactic acid films. Contact conditions: 1-10 days at 40°C. (Reproduced from [63], with permission from Wiley).

FIGURE 2 Overall migration data in ethanol 10% (v/v) and isooctane for PLA and PLA nano-biocomposites. (Reproduced from [64], with permission from Elsevier).

FIGURE 3 (a) Ag ion release from the nanocomposite blown film to food simulant as a function of time and (b) graphical drawing of Ag diffusion-controlled release in the polymer matrix: (A) Ag ions without KT presence and (B) Ag ions attached on and inserted between layered KT. (Reproduced from [67], with permission from Elsevier).

FIGURE 4 Plots of (a) $\ln(m_t/m_\infty)$ versus $\ln(t)$ and (b) m_t/m_∞ versus $t^{1/2}$ for the short-term migration of triacetin from starch acetate films into distilled water. (Reproduced from [70], with permission from Elsevier).

FIGURE 5 Overall migration data in ethanol 10% (v/v) (solid squares) and isooctane (open circles) for PHB and its bionanocomposites. (Reproduced from [76]).

FIGURE 6 Water uptake and water vapour permeability (WVP (a), and overall migration data in ethanol 10% (v/v) and isooctane (b) as a function of CMC-me concentrations for neat PHBV and the nanocomposites. (Reproduced from [77], with permission from RSC Publishing).

TABLE CAPTIONS

TABLE 1 Overall migration in 3% acetic acid and 50% ethanol from the unfilled and the nanocomposite polylactic acid films. Contact conditions: 10 days at 40°C. (Reproduced from [63], with permission from Wiley).

TABLE 2 Specific migration of lactic acid in 3% acetic acid and 50% ethanol from the unfilled and the nanocomposite polylactic acid films. Contact conditions: 10 days at 40°C. (Reproduced from [63], with permission from Wiley).

TABLES

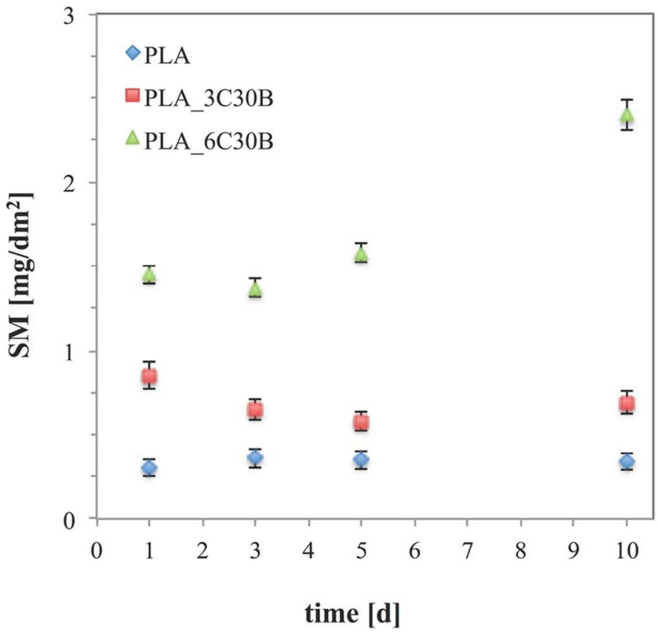
TABLE 1 Overall migration in 3% acetic acid and 50% ethanol from the unfilled and the nanocomposite polylactic acid films. Contact conditions: 10 days at 40°C. (Reproduced from [63], with permission from Wiley).

	Overall migration [mg/dm^2]	
Film sample	3% acetic acid	50% ethanol
Neat PLA	0.5 ± 0.2	0.5 ± 0.2
PLA_3C30B	0.7 ± 0.2	0.5 ± 0.1
PLA_6C30B	0.8 ± 0.3	0.7 ± 0.2

TABLE 2 Specific migration of lactic acid in 3% acetic acid and 50% ethanol from the unfilled and the nanocomposite polylactic acid films. Contact conditions: 10 days at 40°C. (Reproduced from [63], with permission from Wiley).

	Lactic acid specific migration [mg/dm^2]	
Film sample	3% acetic acid	50% ethanol
Neat PLA	n.d.	0.34 ± 0.03
PLA_3C30B	0.25 ± 0.02	0.69 ± 0.05
PLA_6C30B	0.04 ± 0.01	2.40 ± 0.08

n.d., not detectable; PLA, polylactic acid.



Specific migration of lactic acid in 50% ethanol from the unfilled and nanocomposite polylactic acid films. Contact conditions: 1-10 days at 40°C. (Reproduced from [63], with permission from Wiley).
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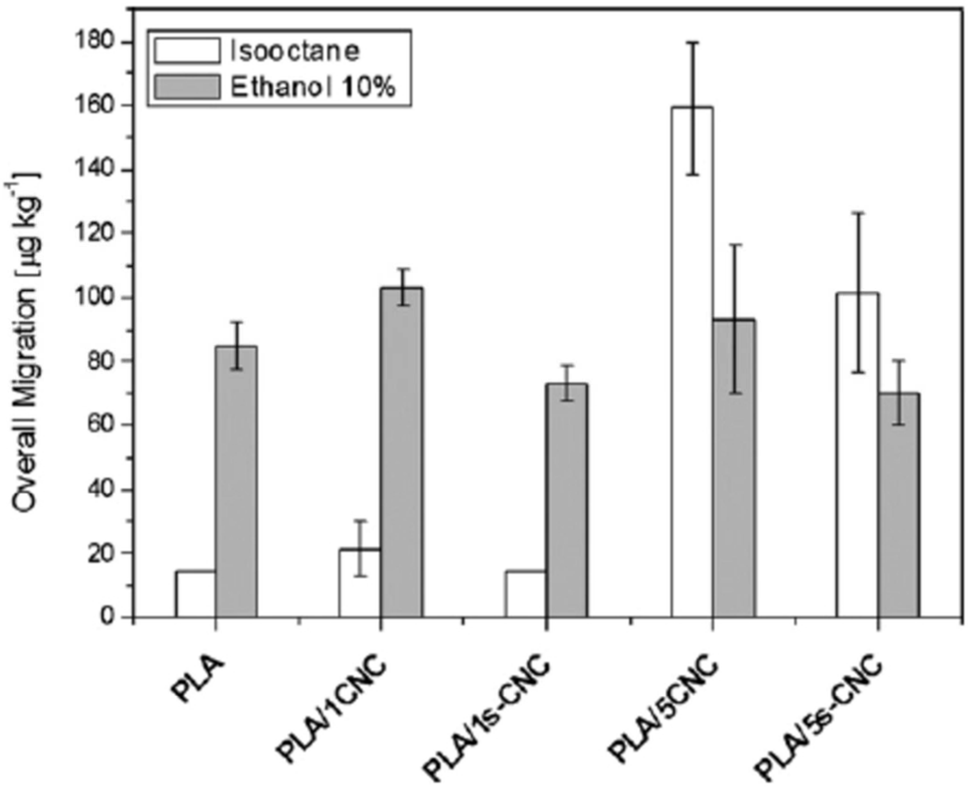

Overall migration data in ethanol 10% (v/v) and isooctane for PLA and PLA nano-biocomposites.
(Reproduced from [64], with permission from Elsevier).
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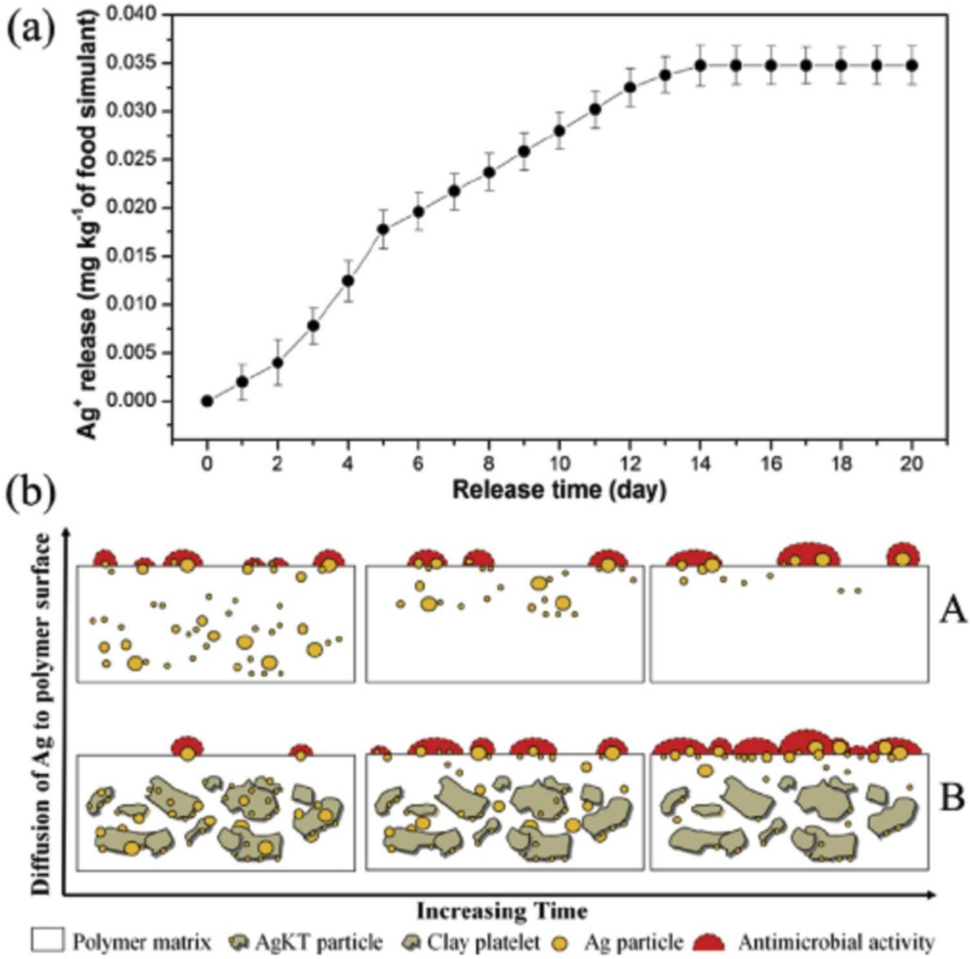

(a) Ag ion release from the nanocomposite blown film to food simulant as a function of time and (b) graphical drawing of Ag diffusion-controlled release in the polymer matrix: (A) Ag ions without KT presence and (B) Ag ions attached on and inserted between layered KT. (Reproduced from [67], with permission from Elsevier).
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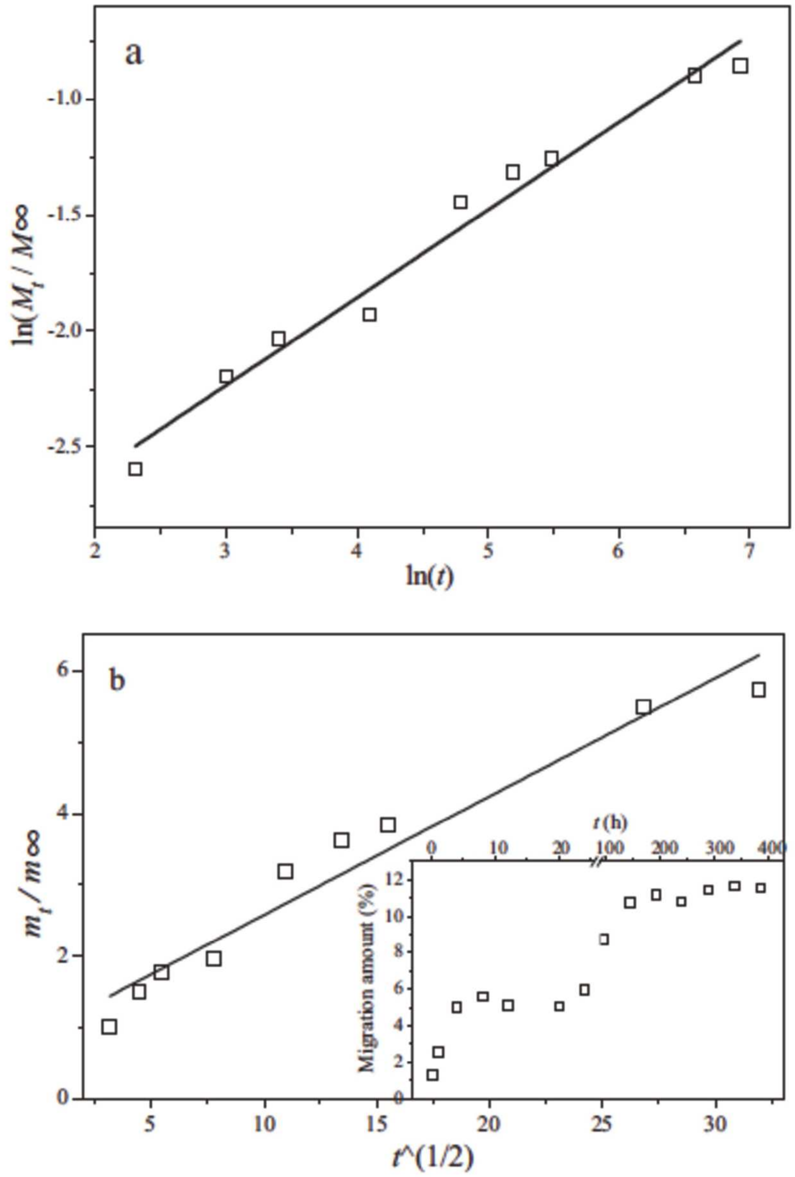
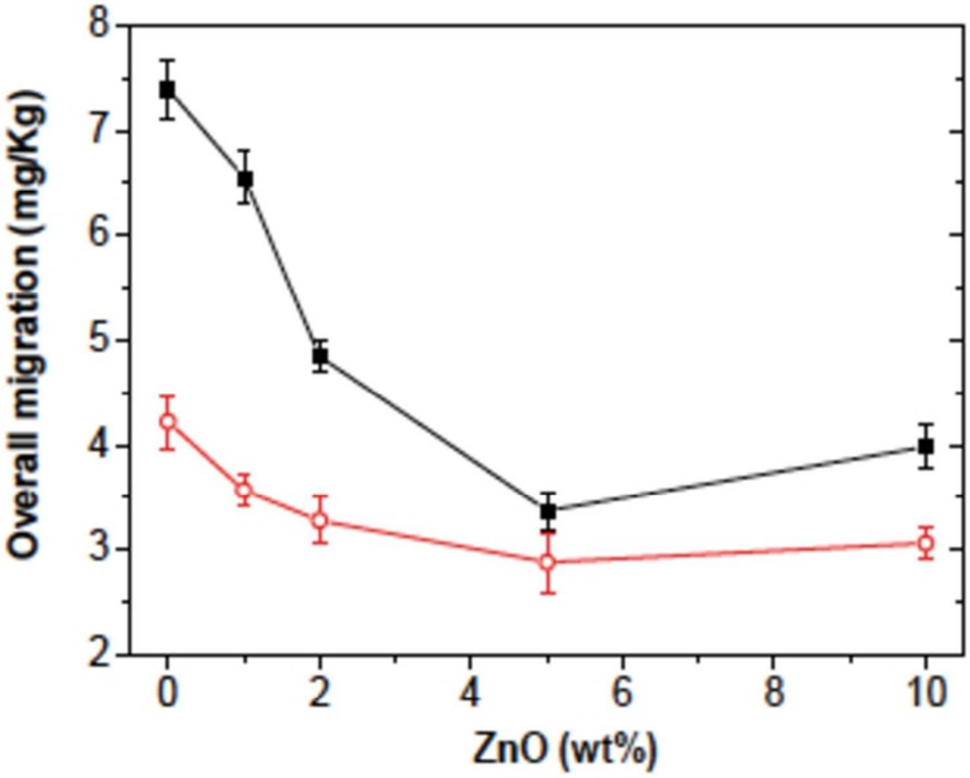


Plots of (a) ln(mt/m∞) versus ln(t) and (b) mt/m∞ versus t1/2 for the short-term migration of triacetin from starch acetate films into distilled water. (Reproduced from [70], with permission from Elsevier).
133x193mm (300 x 300 DPI)



Overall migration data in ethanol 10% (v/v) (solid squares) and isooctane (open circles) for PHB and its bionanocomposites. (Reproduced from [76]).
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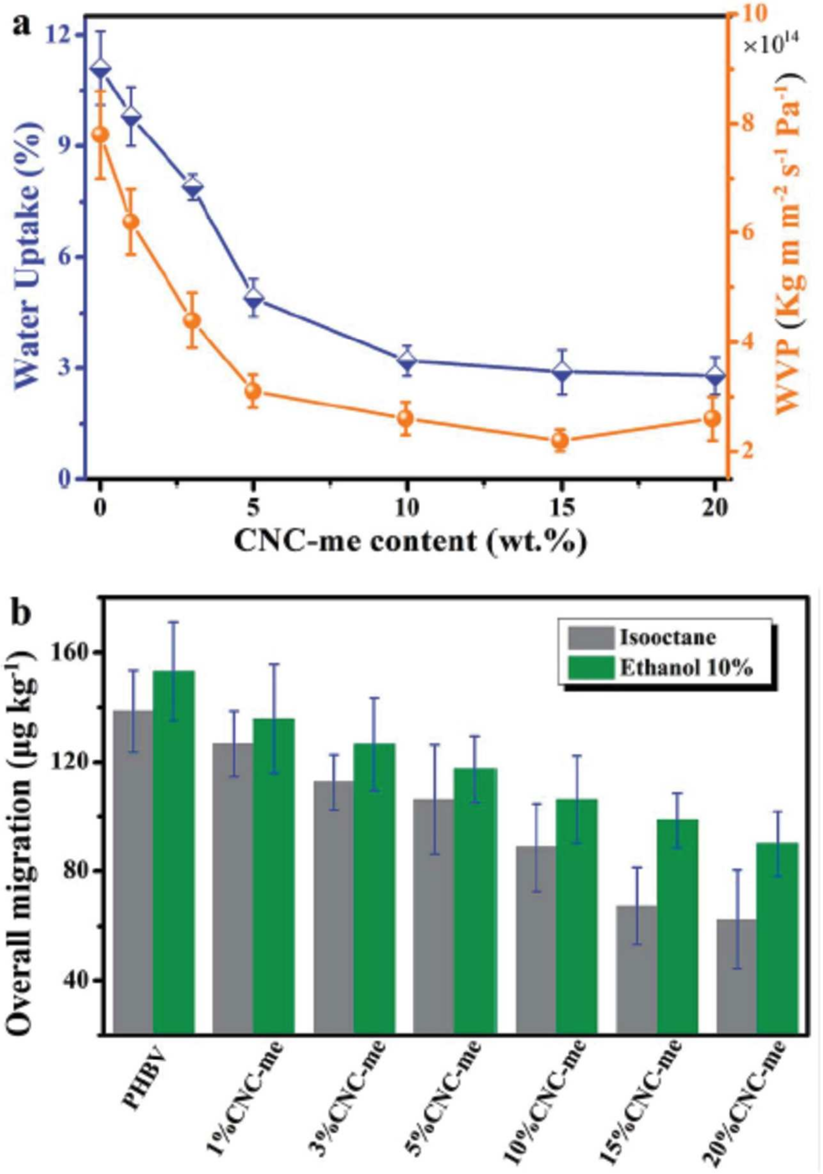

Water uptake and water vapour permeability (WVP (a), and overall migration data in ethanol 10% (v/v) and isooctane (b) as a function of CMC-me concentrations for neat PHBV and the nanocomposites. (Reproduced from [77], with permission from RSC Publishing).
134x189mm (300 x 300 DPI)