

**Special Issue: Manufacturing of Advanced
Biodegradable Polymeric Components**

Guest Editors: Prof. Roberto Pantani (University of Salerno) and
Prof. Lih-Sheng Turng (University of Wisconsin-Madison)

EDITORIAL

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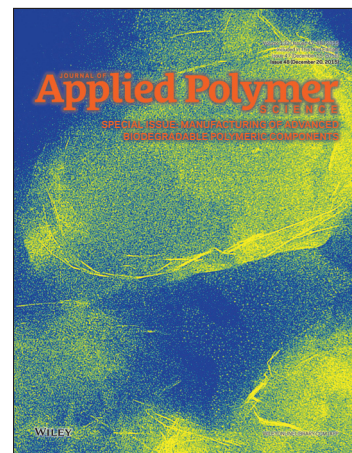
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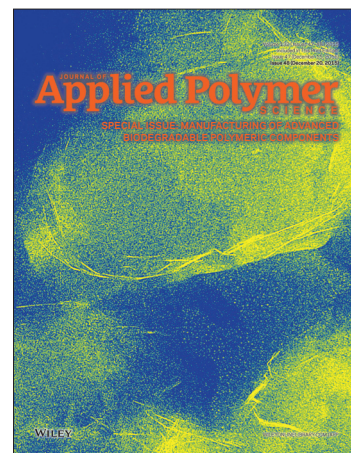
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Recent advances and migration issues in biodegradable polymers from renewable sources for food packaging

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ABSTRACT: In recent years, consumer demand for environmental sustainability and legislative actions has pushed the plastic packaging industry toward biobased plastics. However, despite the advantages related to their ecofriendly nature, the commercial large-scale application of biobased polymers as substitutes for conventional petroleum-derived plastic as packaging materials have been limited up to this point because they show limitations in their processability and material properties performances, especially in terms of their diffusion-barrier properties to small molecules; these are critical for food-contact uses. The main strategies used to overcome these issues involve blending with other biopolymers and/or the addition of other substances, such as microfillers, nanofillers, and plasticizers. In this review, we report on the most recent advances and emerging technologies in food-packaging applications that have potential commercial interest and are based on selected biodegradable polymers from renewable sources. Our particular focus is on issues related to food-packaging interactions and the possible consequent migration of substances. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 42597.

KEYWORDS: biopolymers and renewable polymers; packaging; properties and characterization

Received 18 February 2015; accepted 5 June 2015

DOI: 10.1002/app.42597

INTRODUCTION

In the last few decades, a growing consumer sensitivity toward environmental concerns and an increasing demand for renewable and biobased materials, supported also by legislative actions with respect to environmental protection, sustainability, and waste management, have driven the market toward the development of ecofriendly, biodegradable plastics. The packaging field now contributes over 50% of global biodegradable plastics consumption, and according to a recent study by Smithers Pira,¹ the demand for bioplastics in packaging is expected to rise at an estimated compound annual growth rate of 33% in the period 2013–2023 as the materials become cheaper and improvements in properties lead to a wider variety of possible applications. This trend is driving research toward the development of new and better performing biodegradable systems, often through material modifications, as is well documented by the broad scientific literature available.^{2–17}

Biodegradable polymers can be classified according to the source of their origin, that is, renewable or petrochemical, or according to the method of their production, with the following main categories:¹⁸

- Polymers produced by conventional chemical synthesis from renewable or nonrenewable monomer feedstock, for example,

poly(lactic acid) (PLA), poly(ϵ -caprolactone), poly(butylene succinate), and poly(vinyl alcohol).

- Polymers produced by direct extraction from biomass, for example, polysaccharides, such as starch, chitosan, cellulose, and pectin, and proteins, such as zein, gelatin, casein, soy protein, and wheat gluten.
- Polymers obtained from microorganisms or genetically modified bacteria, for example, polyhydroxyalkanoates (PHAs), including poly(β -hydroxybutyrate) (PHB), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), bacterial cellulose, xanthan, and pullulan.
- Polymers produced by blending, for example, PLA-PHA, starch-PLA, starch-PHB, starch-poly(ϵ -caprolactone), starch-cellulose derivatives, starch-poly(vinyl alcohol), PHA-keratin, chitosan-PLA, and PHB-chitosan.

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 and is degradable by simple hydrolysis of the ester bond.¹⁹ Formed by the polymerization of a controlled

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mixture, in terms of the ratio and sequence of arrangements, of two optical D- or D-isomeric forms of the lactide monomer [i.e., the dimer of lactic acid (LA)], its stereochemical structure can be easily modified to yield a wide spectrum of high-molecular-weight polymers, amorphous or crystalline, with tuned properties.^{19–28} High-molecular-weight PLA, certified as Generally Recognized as Safe by the U.S. Food and Drug Administration, is an odorless, colorless, glossy, stiff, biocompatible, low-toxicity polymer, suitable for direct food contact. It has a very good flavor and aroma barrier, grease resistance to most oils and fats, and properties similar to polystyrene.²⁹ The major use of PLA is in food-packaging applications, mainly for packaged foods with short shelf lives (e.g., yogurts, fruit and vegetables, juice and mineral water) and disposable tableware, and in the pharmaceutical and biomedical fields.^{19,30}

Starch is one of the most abundant natural polysaccharides.³¹ The main agricultural sources for starch production include corn starch, wheat, potato, and cassava.^{32,33} It is composed of two major components: amylose (linear) and amylopectin (branched), whose unit relative content varies depending on the botanical origin of the starch and on the growing conditions; this influences the physicochemical properties of the starch.^{34–37} Native starch is not a thermoplastic material; therefore, starch films are commonly produced by casting, even though starch can also be processed by extrusion technologies after thermoplasticization.^{37–41}

PHAs are polyesters of various hydroxyalkanoates that are naturally synthesized by many bacteria, generally cultivated on agricultural raw materials.^{42,43} Large-scale commercial production of

PHAs uses fermentation technologies. The PHAs are nontoxic and biocompatible and have good UV resistance and physical chemical properties, which are considerably dependent on the monomer composition.^{43–46} The main member of the PHA family is the homopolymer PHB: it is a semicrystalline, isotactic stereoregular polymer with a high level of biodegradability and material properties considered similar to those of polypropylene.

Despite the advantages related to the ecofriendly nature of these polymers, their commercial applications on a large scale to substitute for conventional polymers as packaging materials have been limited up to this point, mainly because all of them present some drawbacks in their properties (mechanical, moisture barrier, thermal, dimensional, etc.). The main critical points concern some limitations in their processability and reduced barrier properties to small molecules such as water and oxygen.^{29,30,34–37,47,48} The last point, in particular, can make biopolymer-based packages limited in effectiveness with respect to the assurance of the adequate quality, safety, and shelf life of the packaged foods to preserve them from deteriorative chemical changes (e.g., nonenzymatic browning; hydrolysis and/or oxidation of lipids, proteins, vitamins, and oligosaccharides and polysaccharides; degradation of natural pigments; etc.), changes in their flavor (due to aroma sorption or transfer of undesirable flavors from the packaging to the food), and migration of substances from the packaging material to the packaged food. Therefore, to improve their performance, blending with other biopolymers and chemical derivatization or addition of other substances such as fillers and plasticizers is generally required. All of these strategies are

Table I. Overall Migration and Specific Migration of LA in 3% Acetic Acid and 50% Ethanol from the Unfilled PLA Films (Neat PLA) and Nanocomposite PLA Films with Cloisite 30B Added at 3 wt % (PLA_3C30B) and 6 wt % (PLA_6C30B)

Film sample	Overall migration (mg/dm ²)		LA specific migration (mg/dm ²)	
	3% acetic acid	50% ethanol	3% acetic acid	50% ethanol
Neat PLA	0.5 ± 0.2	0.5 ± 0.2	Not detectable	0.34 ± 0.03
PLA_3C30B	0.7 ± 0.2	0.5 ± 0.1	0.25 ± 0.02	0.69 ± 0.05
PLA_6C30B	0.8 ± 0.3	0.7 ± 0.2	0.04 ± 0.01	2.40 ± 0.08

The contact conditions were 10 days at 40°C. Reproduced with permission from ref. 84. Copyright 2014 John Wiley & Sons.

currently widely covered in the literature, and a number of compositions based on PLA, starch, and PHAs have been tested; these have resulted to be particularly beneficial with respect to several properties of interest for food-packaging applications.^{4,12,37,38,49–70}

Typical additives that have been investigated include nanofillers such as clays (e.g., natural and quaternary ammonium modified montmorillonite, sepiolite, hectorite, mica, halloysite), Ag zeolites and cellulose nanocrystals (CNCs), metal ions (e.g., silver, copper, gold) and metal oxides (e.g., TiO₂, ZnO, MgO), natural and synthetic antimicrobial or antioxidant agents (e.g., nisin, thymol, carvacrol, α -tocopherol, benzoic acid), and natural plasticizers (e.g., LA, triacetin, triethyl citrate, citric acid, polyols, e.g., glycerol, glycol and sorbitol).⁴

Because there is an abundance of literature dealing with these biodegradable polymers, in this article, we report on the most recent developments and prospects in food-packaging applications of potential commercial interest for selected materials derived from renewable resources based on PLA, starch, and PHAs, focusing attention on the food–packaging interaction issues and the possible consequent migration of substances.^{2–15,71–77}

MIGRATION CONCERNS

In Europe, biodegradable plastics for food-contact applications are regulated in the same manner as conventional plastic materials under Commission Regulation EC 10/2011 on plastic materials and articles intended to come into contact with food. The regulation sets down the safety requirements of plastic materials by giving general provisions and compositional requirements, listing all the substances authorized in the manufacturing of conventional and biodegradable plastics (Annex I) and describing in detail the testing of overall and specific migration (Annex V).⁷⁸ However, because pure biopolymers are in general less stable and have a lower diffusion barrier than conventional polymers, 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 concerning the safety assessment of food packaging made of biodegradable polymers by migration testing have been reported in the literature.

PLA-BASED MATERIALS

The most studied biopolymer is PLA. Migrants from PLA may include LA, the linear dimer of LA (lactoyl lactic acid), other oligomers of PLA (no. 3–13), and the cyclic dimer of LA

(lactide).^{79,80} Among these, LA is included in the list of authorized monomers and other starting substances in European Directive EC 10/2011 with no restrictions or specifications. LA or PLA oligomers are not included. Similarly, in the U.S. Code of Federal Regulations e-CFR 184.1061, the Food and Drug Administration certifies LA as a Generally Recognized as Safe food ingredient and does not provide comments related to LA or PLA oligomers.⁸¹

Migration from pure PLA has been reported to be low.^{79,80,82,83} Mutsuga *et al.*⁷⁹ in 2008 performed LA, lactide, and PLA oligomer 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 to 95°C. LA migration after short-term tests (60°C, 30 min) was detected at levels of 0.008–0.040 mg/dm² from all of the samples in 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 it started to decompose at temperatures above T_g , so the migrant levels increased, particularly for PLA that contained high D-LA levels.

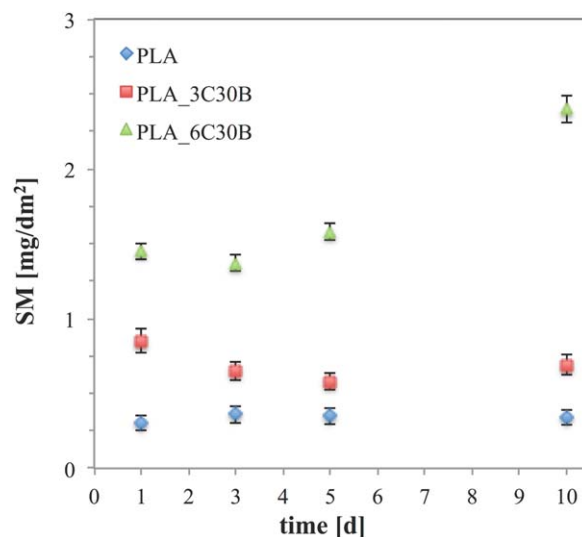


Figure 1. Specific migration of LA in 50% ethanol from the unfilled and nanocomposite PLA films (contact conditions: 1–10 days at 40°C). Reproduced with permission from ref. 84. Copyright 2014 John Wiley & Sons. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

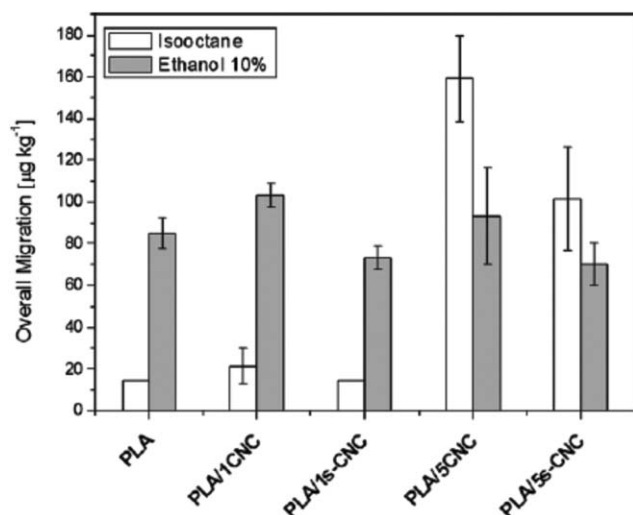


Figure 2. Overall migration data in 10% v/v ethanol and isooctane for the PLA and PLA nanobiocomposites added with 1 wt % and 5 wt % of unmodified cellulose nanocrystals (CNC) and modified cellulose nanocrystals (s-CNC). Reproduced with permission from ref. 85. Copyright 2012 Elsevier.

In the case of food packaging, PLA formulations incorporating plasticizers, stabilizers, nanofillers, and other biopolymers able to improve the properties of the final article may result in a potential modification of the migrational behavior of the PLA. All of these compounds, in fact, have a low weight-average molecular weight with the potential to diffuse through the polymeric matrix when used in packaging or articles in contact with food.¹⁹ Therefore, more studies are needed for its blends and copolymers and also for all of the compounds that are applied or added to improve the physical, mechanical, and barrier properties of PLA.

Di Maio *et al.*⁸⁴ recently developed nanocomposite PLA films added with different amounts (3 and 6 wt %) of Cloisite 30B layered nanoclay having one nanometric dimension and characterized the systems obtained in terms of functional properties and total and LA specific migration in view of food-packaging applications. The films were produced by melt compounding with a laboratory-scale film production pilot plant; this demonstrated that conventional film production technologies are adequate to disperse layered nanofillers in the PLA matrix on a nanoscale with an intercalated–exfoliated morphology. With respect to the unfilled PLA, the developed nanocomposite systems showed improved mechanical performance with marked rises in the modulus and elongation at break and better oxygen-barrier properties with a decrease in the oxygen permeability up to about 61% (from 18.8 ± 2.6 to $7.3 \pm 0.4 \text{ cm}^3 \text{ mm m}^{-2} \text{ d}^{-1} \text{ bar}^{-1}$) for the film with 6 wt % nanoclay added. In view of food-packaging applications, the authors also verified that the migration behavior of the nanocomposite PLA met the safety requirements set down by legislation for food-contact plastics, according to the most recent European Union regulation (EC 10/2011), which authorizes on a case-by-case basis the use of engineered nanosized particles as additives for food-packaging materials.⁷⁸ With this aim, total and LA specific migration tests were performed with aqueous-based simulants, selected as a worst case for the potential migration from PLA (Table I). In

particular, 3% acetic acid, a simulant for the acidic character of foods, and 50% ethanol, a simulant for migration in milk and dairy foods, were considered. The results obtained demonstrate that the PLA films added with Cloisite 30B nanoclay at the loadings used in the study showed overall migration levels comparable to the neat PLA and ranging between 0.5 and 0.8 mg/dm^2 , well below the migration limit of 10 mg/dm^2 as set down by EC 10/2011 regulation, both in the acidic and the aqueous simulant. Instead, the LA specific migration levels show a different trend depending on the kind of contacting solvent: in the case of 3% acetic acid they always remained very low, near to the detection levels, whereas in the case of 50% ethanol they increased with the amount of Cloisite 30B nanoclay added to the film samples, according to the data plotted in Figure 1, while remaining much lower than the applicable generic specific migration limit (60 mg/kg food or 10 mg/dm^2).⁷⁸ The higher swelling capability of 50% ethanol toward PLA compared with the 3% acetic acid was responsible for the higher specific migration levels of LA in the alcoholic simulant.

Fortunati *et al.*⁸⁵ investigated the effect of pure and modified CNCs on the properties of PLA nanobiocomposites produced by solvent casting, focusing their attention on the changes in gas transport and overall migration behavior. They found that both the unmodified and modified CNCs had a positive influence on the barrier properties of the nanobiocomposites, which improved as a consequence of the higher tortuosity of the penetrant molecule pathway across the PLA matrix; this was induced by the nanofiller addition. The effects were more relevant when modified CNCs were used because of the better interaction of the nanofillers with the polymer matrix. In particular, compared to the neat PLA films, the PLA-based films with 5 wt % modified CNCs added gave the highest reduction in the oxygen transmission rate (OTR) of about 48% (the values of OTR with film thickness decreased from 30.5 ± 1.0 to $15.8 \pm 0.6 \text{ cm}^3 \text{ mm m}^{-2} \text{ d}^{-1}$), whereas those with 1 wt % modified CNCs added showed the highest reduction in the water vapor permeability (WVP) of about 34% (WVP passed from 1.04×10^{-14} to $0.69 \times 10^{-14} \text{ kg m s}^{-1} \text{ m}^{-2} \text{ Pa}^{-1}$). In terms of the migrational behavior, overall migration tests, performed according to the EC 10/2011 regulation with 10% v/v ethanol (simulant A) and isooctane (alternative simulant to D2) as liquid food simulants, demonstrated that PLA maintained negligible migration levels even in the presence of both unmodified and modified CNCs (Figure 2). Both pure PLA and PLA-based composite systems with CNCs added at 1 wt % showed higher migration levels in 10% ethanol than in isooctane because the alcohol swelled the polymer and thus promoted migration. However, in PLA systems with CNCs added at 5 wt %, the plasticizing action of the alcohol in the presence of the CNCs promoted structural rearrangement of the polymer chains during incubation in ethanol and so affected the migration process. As a result, these systems show higher migration levels in isooctane than in 10% ethanol. Again, at a fixed CNC loading, the overall migration was lower in the presence of modified CNCs because of better polymer–filler interactions. The maximum overall migration was 0.16 mg/kg in isooctane for the composite of PLA added with 5 wt % unmodified CNCs. This value was well below the

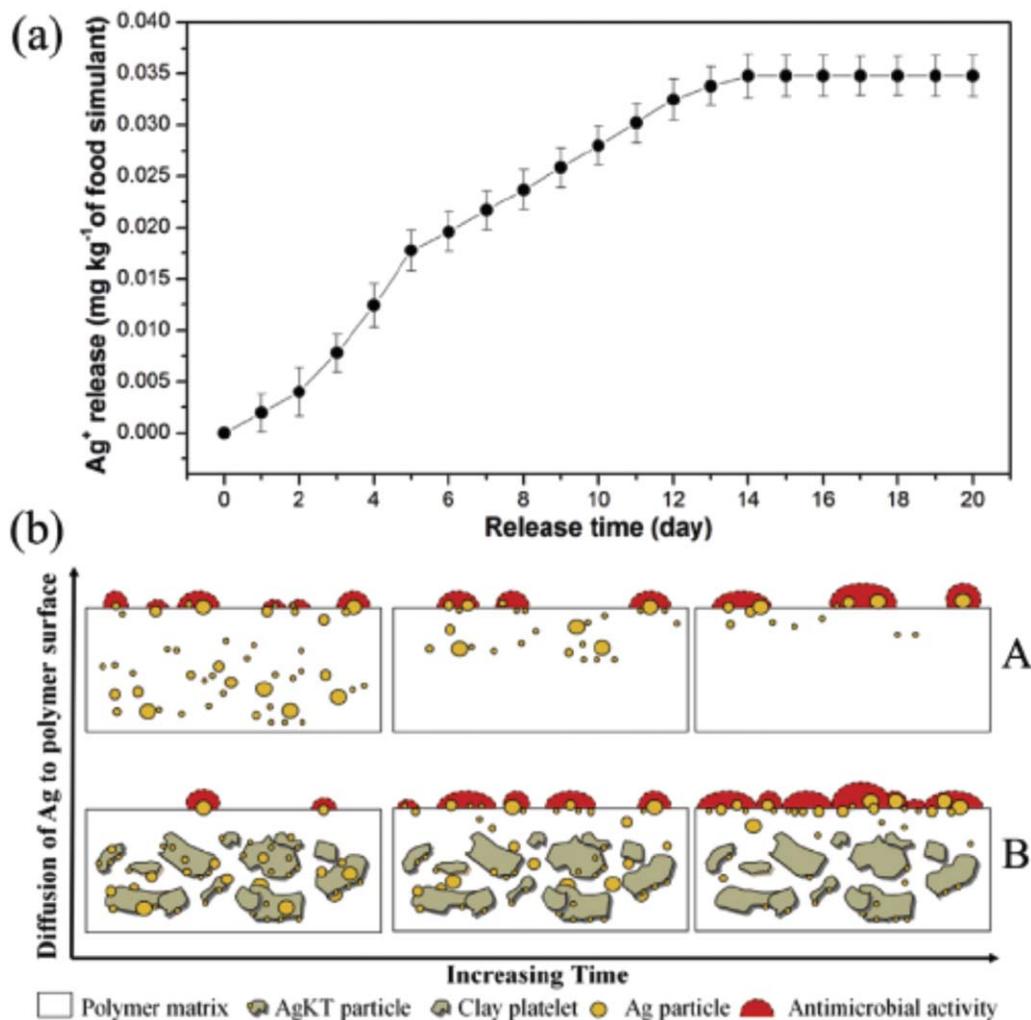


Figure 3. (a) Ag-ion release from a PLA-based nanocomposite blown film to a food simulant as a function of the time and (b) graphical drawing of the Ag diffusion-controlled release in the polymer matrix. (A) Ag ions without kaolinite and (B) Ag ions attached to and inserted between layered kaolinite. Reproduced with permission from ref. 88. Copyright 2014 Elsevier. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

applicable generic migration limit of 60 mg/kg food in the EC 10/2011 regulation.

In a subsequent article, Fortunati *et al.*⁸⁶ analyzed the effect of the same unmodified and modified CNCs in combination with Ag nanoparticles on the barrier and migration properties of the PLA nanobiocomposites produced by solvent casting and intended to be used as active food packaging. The authors demonstrated that the addition of the Ag nanoparticles in combination with the modified CNCs produced the transport of oxygen and water vapor comparable to those of binary PLA/CNC systems. No samples exceeded the overall migration limits in 10% ethanol and isooctane, even when the migration levels are higher in the ternary blends than in the binary formulations without Ag nanoparticles. The specific migration of nanosilver in both simulants was also evaluated to ascertain the compliance with the specific migration limit of 0.05 mg of silver/kg of food currently referenced by the European Food Safety Authority (EFSA).⁸⁷ In general, the amount of silver released from different ternary blends increased with the CNC loading, and at a

fixed CNC percentage, it was higher in the formulations containing the modified CNCs than the unmodified ones. However, the Ag⁺ specific migration was always well below the limit indicated by the EFSA when the simulant was isooctane (the highest specific migration of Ag⁺ in isooctane was 0.023 mg/kg for the ternary sample added with 5 wt % modified CNCs and 1 wt % Ag nanoparticles). On the contrary, it exceeded the permitted limits when the simulant was 10% v/v ethanol for both ternary formulations containing the modified CNCs (the Ag⁺ specific migration values were 0.061 ± 5 and 0.087 ± 7 mg/kg for the ternary samples added with 1 and 5 wt % modified CNCs, respectively) as a consequence of the plasticization of the PLA matrix in the ethanolic simulant; this made the migration of Ag⁺ easier.

Girdthep *et al.*⁸⁸ developed biodegradable nanocomposite blown films based on compatibilized PLA/poly(butylene adipate-co-terephthalate) and silver-loaded kaolinite (AgKT) for use as a model package for dried fruits. They found that in systems compatibilized with tetrabutyl titanate, AgKT enhanced the

gas-barrier properties of the films with respect to the neat PLA/poly(butylene adipate-co-terephthalate) polymer blend, giving a reduction of about 50% of both water vapor and oxygen permeability. In particular, the water vapor permeance decreased from 2.74 ± 0.20 to $1.22 \pm 0.04 \text{ g m}^{-2} \text{ d}^{-1} \text{ mmHg}^{-1}$, and OTR decreased from 600.00 ± 150.00 to $369.35 \pm 5.59 \text{ cm}^3 \text{ m}^{-2} \text{ d}^{-1}$. Moreover, they measured Ag particle migration in slightly acidified water solutions containing acetic acid at 4 wt %, chosen as simulant solution according to EFSA (EFSA 2004, 2005, 2006, and 2007) and Thai Industrial Standards (TIS 1027–2553) and found that AgKT inhibited bacterial growth on the polymer film as a result of the action of Ag nanoparticles and allowed the control of Ag release for a long-lasting antibacterial effect and so saved the product quality. In particular, as shown in Figure 3, the compatibilized PLA/PBAT/tetrabutyl titanate/AgKT nanocomposite films showed a rapid initial release rate of Ag ions ($0.0036 \text{ mg kg}^{-1} \text{ d}^{-1}$ within the first 5 days), controlled only by diffusion, followed by a decreased release rate ($0.0021 \text{ mg kg}^{-1} \text{ d}^{-1}$ during days 5–14); this was potentially related to both Ag-ion diffusion through the matrix and tortuous paths of kaolinite layers hindering the ion migration. The concentration of released Ag ions at day 14 onward remained stable at about 0.0348 mg/kg . Such Ag migration complied with the limits as determined by EFSA and TIS standards (0.05 and 100 mg/kg , respectively) for plastic bags in contact with food. Accordingly, the developed nanocomposite film could be used safely as an Ag-based package in contact with food.

Mattioli *et al.*⁸⁹ proposed the use of a deposition technology to improve the barrier properties of PLA films and analyzed the gas barrier and overall migration of PLA films coated with hydrogenated amorphous carbon layers (a-C:Hs) deposited with a radiofrequency plasma deposition method with different exposure times (5, 20, and 40 min). The authors observed a significant reduction in the OTR and WVP values for all of the PLA/a-C:H films with respect to the untreated PLA. In particular, they obtained a reduction in the OTR values of about 59% (OTR with film thickness passed from 30.5 ± 1.0 to $12.6 \pm 3.2 \text{ cm}^3 \text{ mm m}^{-2} \text{ d}^{-1}$) and a reduction in the WVP values of about 68% (WVP passed from 1.04×10^{-14} to $0.33 \times 10^{-14} \text{ kg m s}^{-1} \text{ m}^{-2} \text{ Pa}^{-1}$) in the case of PLA/a-C:H treated for 5 min, whereas 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 field emission scanning electron microscopy and X-ray photoelectron spectroscopy 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 European Union legal standards (EC 10/2011) with 10% v/v ethanol and isooctane as food simulants. The tests demonstrated that for all of the film samples, the migration levels in 10% v/v ethanol, which plasticized the PLA, was higher than in isooctane, although they always remained well below the limit of 60 mg/kg . Only in the case of PLA/a-C:H treated for 5 min was a beneficial effect of the coating layer on the overall migration value in 10% v/v ethanol

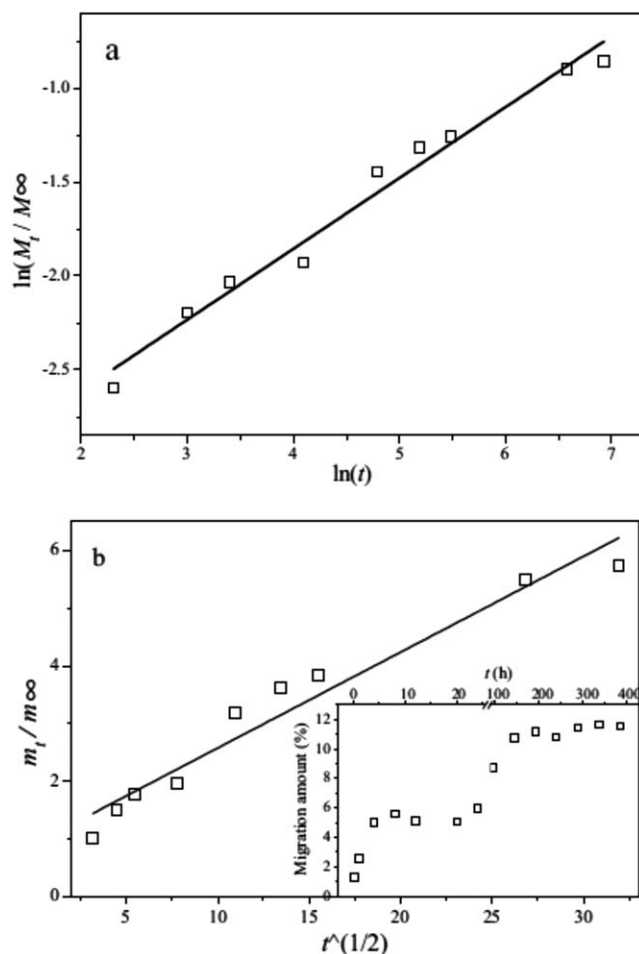


Figure 4. Plots of (a) $\ln m_t/m_\infty$ versus $\ln t$ and (b) m_t/m_∞ versus $t^{1/2}$ for the short-term migration of triacetin from starch acetate films into distilled water. Reproduced from ref. 90. Copyright 2014 Elsevier.

observed. For the PLA/a-C:H films deposited at longer exposure times, the overall migration values strongly increased with the a-C:H thickness, especially in the case of 40 min of a-C:H deposition, where deeper and wider microcracks were present.

STARCH-BASED MATERIALS

With respect to 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 temperatures and to thermoplasticize the polymer, especially when the food has a high affinity (i.e., strong interaction) with the polymer.

Zhu *et al.*⁹⁰ analyzed the migration and the associated structural changes of hydrophobic starch acetate films plasticized with triacetin during contact with distilled water for different time periods; this demonstrated that the triacetin migration was a concentration-driven process, fast at the beginning and slow after, which could be described by an overall first-order kinetic model ($R^2 = 0.9324$). A similar first-order kinetic model was demonstrated to be adequate for describing the migration of three natural antimicrobial agents (thymol, carvacol, and linalool) into isooctane from starch-based films even by other

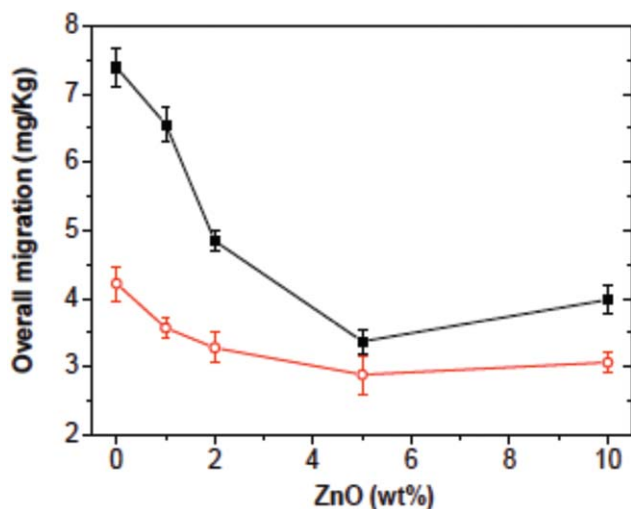


Figure 5. Overall migration data in 10% v/v ethanol (■) and isoctane (○) for PHB and its bionanocomposites. Reproduced with permission from ref. 96. Copyright 2014 MDPI AG. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

authors.⁹¹ Zhu *et al.*⁹² also analyzed the migration results by means of a diffusion model, either a short term ($m_t/m_\infty < 0.67$) or 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 m_t is the amount of triacetin migrated at time t , m_∞ is the amount of triacetin migrated from the film at equilibrium, k is a constant that characterizes the polymer network system and n is the diffusional exponent characteristic of the release mechanism. The estimated value of n , obtained from the slope of the $\ln m_t/m_\infty$ versus $\ln t$ plot, as shown in Figure 4(a), was equal to 0.3776 ($R^2 = 0.9765$); this demonstrated that the short-term migration of triacetin could be predominantly described by a Fickian diffusion mechanism (i.e., $n \leq 0.5$) and was scarcely affected by the relaxational phenomena because of the diffusion of the solvent and plasticizer within the film matrix. At longer times, the observed sigmoidal shape of the curve [see the inset in Figure 4(b)] for the subsequent migration of triacetin suggested a change in the diffusion model that becomes non-Fickian because the subsequent migration of triacetin was affected by the structural changes of the starch acetate film matrix, as revealed by Fourier transform infrared spectroscopy and small-angle X-ray diffraction analyses. In particular, the migration of triacetin increased with 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 intermolecular interaction between triacetin and starch acetate was weakened, and thus, the intermolecular and intramolecular interaction of starch acetate molecules was directly enhanced. This gave a more compact aggregation structure within the film matrix.

The same authors in a subsequent article 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 multiscale structures

(crystalline structure and ordered aggregation structure) of the starch ester film.⁹³ They demonstrated that the microwave heating accelerated the triacetin migration from the starch ester film to the milk system, compared with simple immersion at 30°C without microwaves. The phenomenon was attributed to the film structural changes, that is, the enlargement of the inter-chain distances in the amorphous region, partial destruction of the crystallite structure, and shrinkage of the ordered microregions.

PHA-BASED MATERIALS

Studies on the migration behavior of PHAs to our best knowledge are rare and limited to the measurement of overall migration. Bucci *et al.*⁹⁴ 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 with four different food simulant solvents (distilled water, 3% acetic acid, 15% ethanol, and heptane). The authors verified that in all cases, the results were below the limit recommended by Resolution 105/99; this was 8.0 mg/dm² or 50 mg/kg, and they hypothesized that the residue might have been monomers

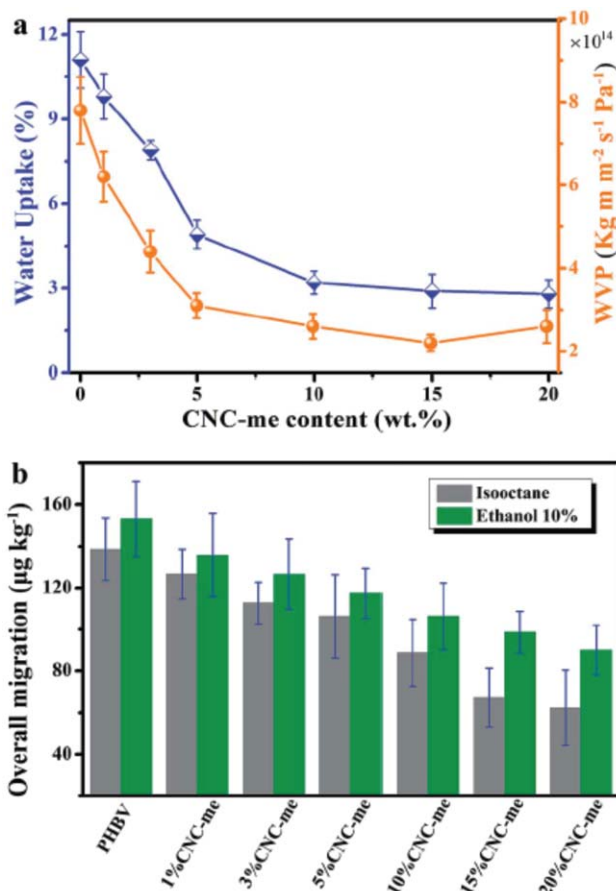


Figure 6. (a) Water uptake and WVP and (b) overall migration data in 10% v/v ethanol and isoctane as a function of the CNC-me concentration for the neat PHBV and nanocomposites. Reproduced with permission from ref. 97. Copyright 2014 RSC Publishing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Water Vapor, D-Limonene, and Oxygen Permeability Values of the Multilayer PHBV-Based Films with and without Electrospun Zein Nanofibers as the Inner Layer

Zein deposition time	WVP $\times 10^{15}$ (kg m ⁻¹ Pa ⁻¹ s ⁻¹)		Limonene permeability $\times 10^{15}$ (kg m ⁻¹ Pa ⁻¹ s ⁻¹)		Oxygen permeability $\times 10^{19}$ (m ³ m m ⁻² s ⁻¹ Pa ⁻¹)	
	Compression molding	Casting	Compression molding	Casting	Compression molding	Casting
Control	3.83 \pm 0.08 ^{a,1}	50.40 \pm 6.00 ^{a,2}	2.73 \pm 0.37 ^{a,1}	22.80 \pm 5.33 ^{a,2}	15.40 \pm 0.15 ^{a,1}	14.61 \pm 0.42 ^{a,1}
10 min	3.39 \pm 0.14 ^{a,1}	14.00 \pm 8.03 ^{b,2}	3.18 \pm 0.18 ^{a,1}	15.10 \pm 0.86 ^{b,2}	11.40 \pm 0.41 ^{b,1}	11.10 \pm 0.52 ^{b,1}
20 min	4.04 \pm 0.51 ^{a,1}	16.00 \pm 8.00 ^{b,2}	1.82 \pm 0.44 ^{b,1}	13.80 \pm 4.28 ^{a,b,2}	6.06 \pm 0.22 ^{c,1}	8.12 \pm 0.15 ^{c,1}
60 min	2.35 \pm 0.56 ^{b,1}	3.94 \pm 0.05 ^{c,2}	1.44 \pm 0.33 ^{b,1}	6.41 \pm 1.27 ^{c,2}	3.73 \pm 0.20 ^{d,1}	6.17 \pm 0.12 ^{d,2}

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^{a-d}Different superscripts within the same column indicate significant differences among formulations ($p < 0.05$).

^{1,2}Different superscripts within the same line indicate significant differences due to the method used ($p < 0.05$).

released in the PHB production process or additives used in the plastics manufacturing processes, such as a white pigment or a mold-release agent used in the injection process.⁹⁵

Recently, other studies have been focused on the overall migration of PHB-based nanocomposite films.^{96–100}

Díez-Pascual *et al.*⁹⁶ prepared PHB-based bionanocomposites incorporating different contents of ZnO nanoparticles and analyzed their barrier, antibacterial, and migration properties. The authors found that the water uptake and WVP of the nanocomposites decreased with increasing ZnO content by up to 66 and 38%, respectively, at 5.0 wt % nanoparticle content in comparison to the neat biopolymer. They related this enhanced behavior to the higher crystallinity 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 5 wt % ZnO, probably because nanofillers started to aggregate at higher ZnO contents. The antibacterial activity, instead, progressively increased with the nanofiller concentration. In terms of migration, overall migration tests with nonpolar (isooctane) and polar (10% v/v ethanol) simulants demonstrated that the total amount of migrated substances significantly decreased with increasing nanoparticle content up to 5 wt % ZnO and 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.*⁹⁷ developed a transparent nanocomposite-based packaging film comprised of PHBV and different concentrations of functionalized CNCs [cellulose nanocrystal methyl ester (CNC-me) added at 1–20 wt %] and evaluated the water-barrier and migration properties. The authors observed a noticeable reduction in liquid water uptake and WVP values with increasing CNC-me concentration compared to neat PHBV (Figure 6). The obtained improvements were larger than those reported for ZnO, multiwalled carbon nanotubes, or carbon nanofiber-reinforced PHBV.^{98–100} Also the overall migration, evaluated both in isooctane and 10% v/v ethanol, was found to progressively decrease in systems incorporating increasing amounts of CNC-me into the polymer matrix. All of the reported results were attributed to the good interfacial adhesion between PHBV

and the CNC-me nanofiller and the increased crystallinity of the nanocomposites, according to other literature findings on similar systems.^{101,102} In particular, an effective nucleating action, resulting in a promotion of the heterogeneous nucleation, the overall crystallization rate, and the crystal perfection of the polymer matrix, was also reported elsewhere for different PHBV/CNC/Ag and PLA/CNC/Ag nanocomposites containing homogeneously dispersed CNC/silver nanohybrids below 10 wt % loading; the resulting refined crystal structure gave obvious improvements in the mechanical and barrier properties. No further beneficial effects were found at higher filler loadings because the nucleating effect was weakened because of the aggregation phenomena of CNC/Ag; this resulted in a slight reduction of the polymer crystallinity.

COMPOSITE AND MULTILAYER SYSTEMS

Recently, Fabra *et al.*¹⁰³ prepared multilayered PHBV-based films by casting and compression-molding; these contained as the inner layer electrospun zein nanofibers able to improve the barrier properties of the structure with minimum changes in the mechanical and optical properties. In particular, they analyzed the effects of both the film structure and film-processing technique on the barrier properties to small molecules of relevant interest for food quality and preservation: water vapor, oxygen, and D-limonene. The latter is the most extensively studied aroma compound with respect to its sorption by polymers, is known as a precursor of off-flavor compounds, and is usually used as the standard permeant molecule for testing the aroma barrier.¹⁰⁴ Their results, reported in Table II, demonstrate that in general, the structures prepared by compression molding, in which the polymer chains were more compacted and give rise to a denser structure, were less permeable to water vapor and limonene than their counterparts prepared by casting. On the other hand, the oxygen permeability values were very similar in both structures. Moreover, in all of the systems, the resistance to mass transfers increased with the electrospun fiber deposition time through an increase in the zein interlayer thickness, as expected. In particular, for the longest deposition time, the films prepared by compression molding showed a reduction in the permeability up to 38% for water vapor, 47% for D-limonene, and 76% for oxygen.

Similar advantages on the barrier properties to oxygen, D-limonene, and water vapor were also found by Pardo-Ibáñez *et al.*¹⁰⁵ on keratin–PHA melt-compounded composites added with 1 wt % keratin.

Another strategy recently considered to improve some technological properties of biopolymers, primarily the barrier performances, is the development of multilayer film systems, mainly based on PHA and PLA.^{106,107} In this field, the work of Boufariguine *et al.*¹⁰⁷ was very original. The authors produced novel multilayer laminates of PLA with a small amount of PHBV (10 wt %) with a custom multilayer coextrusion laboratory-scale plant that allowed the multiplication of the number of alternate layers of PLA and PHBV within a film. The films obtained with processing conditions were optimized to give a well-developed lamellar morphology showed an increased ductility and gas-barrier properties compared with neat PLA and classical blending methods. In particular, compared to the neat PLA, the films containing 129 theoretical layers showed an elongation at break of 52%, almost three times greater, and a helium permeability close to $7.4 \times 10^{-17} \text{ m}^3 \text{ m m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ and approximately 40% lower. However, helium is a neutral gas, whose small molecules are prevented from any possible interaction within the polymer matrix. Therefore, even if the proposed method appeared promising to create multilayer biodegradable structures with improved barrier properties, the reported beneficial effects could not be extrapolated to more interactive molecules qualitatively because often good gas-barrier systems are mediocre barriers to the movement of other penetrants (e.g., vapors, aromas, plasticizers).¹⁰⁸

CONCLUSIONS AND PROSPECTS

In this review, we discussed the most recent advances and the main research efforts regarding diffusion barrier improvements, food–packaging interaction issues, and possible consequent migration of substances of selected biobased and biodegradable polymers for food-packaging applications. In particular, we looked at the state of the art of PLA, starch, and PHAs, which are the most interesting from a commercial point of view and show the greatest growth in market share. The reviewed literature primarily focused on novel formulations based on the addition of other substances, such as microsized and nanosized fillers and plasticizers, intended to overcome the limitations of such biopolymers, in terms of the processability, stability, and structural and functional performance. These formulations have been demonstrated to be effective for improving several properties of technological interest, mainly the diffusion barrier against the permeation of low molecules, such as water and oxygen, without unacceptable detrimental effects toward the 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 of the effect on human health and risk assessments are largely insufficient, especially when nanosized additives are contained in the biopolymer formulation. Therefore, even when the research continues into different types of fillers and functional additives and the allowance of new materials and systems with a great variety of property profiles and continuously

improved properties to compete in terms of the cost and performance with conventional polymers in several specific applications, the actual use of these systems will only be possible after more conclusive results ensure that the safety of this kind of packaging materials in direct food-contact applications will be achieved. Overall and specific migration of all of the possible harmful migrating substances (nanofillers, plasticizers, antimicrobial additives, etc.) must again be investigated thoroughly under different testing conditions to demonstrate that these novel biodegradable packages meet the legal requirements.

ACKNOWLEDGMENTS

Part of this study was performed with financial support from Project PON 01_01409 entitled “Innovazioni di processo e di prodotto per incrementare i profili di sicurezza e per diversificare la gamma dei prodotti (freschi e stagionati) a base di carne suina (SAFEMEAT)”.

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