

Biodegradable active materials containing phenolic acids for food packaging applications

Ramón Ordoñez  | Lorena Atarés | Amparo Chiralt

Instituto Universitario de Ingeniería de Alimentos para el Desarrollo, Universitat Politècnica de València, Valencia, Spain

Correspondence

Ramón Ordoñez, Instituto Universitario de Ingeniería de Alimentos para el Desarrollo, Universitat Politècnica de València, Camino de Vera, s/n, 46022 Valencia, Spain.
Email: raorla@doctor.upv.es

Funding information

Ministerio de Ciencia e Innovación, Grant/Award Numbers: AGL2016-76699-R, PID2019-105207RB-I00

Abstract

The development of new materials for food packaging applications is necessary to reduce the excessive use of disposable plastics and their environmental impact. Biodegradable polymers represent an alternative means of mitigating the problem. To add value to biodegradable materials and to enhance food preservation, the incorporation of active compounds into the polymer matrix is an affordable strategy. Phenolic acids are plant metabolites that can be found in multiple plant extracts and exhibit antioxidant and antimicrobial properties. Compared with other natural active compounds, such as essential oils, phenolic acids do not present a high sensorial impact while exhibiting similar minimal inhibitory concentrations against different bacteria. This study summarizes and discusses recent studies about the potential of both phenolic acids/plant extracts and biodegradable polymers as active food packaging materials, their properties, interactions, and the factors that could affect their antimicrobial efficiency. The molecular structure of phenolic acids greatly affects their potential antioxidant and antimicrobial capacity, as well as their specific interactions with polymer matrices and food substrates. These interactions, in turn, can lead to plasticizing or cross-linking effects. In the present study, the antioxidant and antimicrobial properties of different biodegradable films with phenolic acids have been described, as well as the main factors affecting the active properties of these films as useful materials for active packaging development. More studies applying these active materials in real foods are required.

KEYWORDS

active packaging, antimicrobial, antioxidant, sustainability, food safety

1 | INTRODUCTION

In the search for environmentally responsible operations, bioplastic-based materials have shown potential for replacing traditional plastics in the food packaging industry due

to their renewable origin and/or biodegradability (Choi et al., 2018; F. Zhu, 2021). On the other hand, active packaging is a novel approach aimed at developing packaging materials that also carry active agents to improve food quality and safety (Woranuch et al., 2015). These agents'

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functionalities could be nutrient supplementation, antimicrobial or antioxidant activity, and more (Cheng et al., 2015; Fabra et al., 2011). Active materials could perform either by interacting with the food or with the headspace in the container (Sung et al., 2013). These materials have been widely studied as a means of extending food shelf life while reducing the use of synthetic chemical preservatives, as demanded by consumers who prefer additive-free, natural food products. Some studies have reported accumulations of these compounds along the food chain, which could become harmful for consumer health or lead to the development of microbial resistance (Guil-Guerrero et al., 2016; Jaiswal & Jaiswal, 2015). Naturally occurring compounds, such as essential oils (EOs), phenolic acids (PA), and other plant metabolites, are considered to be highly promising alternatives to synthetic preservatives (Guil-Guerrero et al., 2016).

There are numerous previous studies on active packaging materials using EOs or their main compounds as natural preservatives on the basis of their antimicrobial and antioxidant properties. EO and their main compounds have been reported not only as good antimicrobial agents themselves but also as effective additives in bioplastic films (Tampau et al., 2018). Requena et al. (2019b) studied the minimum inhibitory concentration (MIC) of several of the main compounds of EO in both Gram-positive and Gram-negative bacteria, reporting values between 0.5 and 1.75 mg/ml, with cinnamaldehyde being the most active (0.5 mg/ml for both types of bacteria). Carvacrol and thymol also presented MIC values below 1 mg/ml, and a promising synergistic effect of carvacrol and cinnamaldehyde was also reported. The effect of EO compounds on the organoleptic properties of food products is the main drawback that greatly limits their application in food products (Atarés & Chiralt, 2016). Sapper et al. (2020) reported a great persistence of the flavor and aroma of carvacrol in apples coated with polyvinylalcohol–starch–carvacrol-based coatings, which negatively affected the sensorial acceptance.

PA are naturally occurring compounds mostly derived from benzoic or cinnamic acids. They play a major role in the natural defense of plants against viruses and fungal and bacterial species (Heleno et al., 2015). As plant metabolites, they can be found in multiple natural extracts linked to consumer health benefits (Rashmi & Negi, 2020). The antioxidant and antimicrobial properties of PAs have been widely studied (Kumar & Goel, 2019; Wang et al., 2019), and some of them have shown great potential as food preservatives. Because of these properties, as well as the reported potential health benefits (Rashmi & Negi, 2020), PAs could be effective active agents when looking to obtain active food packaging. Nevertheless, their sensory impact when applied as food additives or active com-

pounds in packaging materials needs to be evaluated. In contrast to the highly negative sensory impact produced by EOs, organoleptic modifications occur to a much lower extent with PAs (Meira et al., 2017; Miyague et al., 2015).

Active packaging materials that incorporate substances that are intended to be released into food should comply with the requirements of authorization under specific legislation on food, such as legislation on food additives (European Union, 2009). The incorporation of PAs as food additives is not generally contemplated, although these are usual components of many food products and have recognized health properties (Rashmi & Negi, 2020). In the United States, the Food and Drug Administration classifies as generally recognized as safe numerous phenol-rich plant extracts such as grape pomace, cranberry, or coffee. Tannic and cinnamic acids are listed as flavoring and adjuvant agents. In Europe, natural plant extracts fall under Directive 2002/46/EC (Martillanes et al., 2017). Some specific compounds have already been approved for different uses. Carminic acid (E-120) is a widely used colorant, and benzoic acid (E-210) is used as a preservative. Recent research on phenolic compounds demonstrates their potential as natural preservatives to be applied to highly perishable products. Given that these compounds represent a promising alternative to synthetic additives, more work is needed to determine their maximum daily intake for safe application in food products.

The objective of this study is to analyze the reported studies on PAs or plant extracts rich in these compounds in terms of their antimicrobial or antioxidant capacity when incorporated into biodegradable polymeric materials and, therefore, their potential for the food packaging industry. The different biodegradable polymers available for food packaging are summarized as well as the main studies on the antimicrobial and antioxidant properties of these phenolic compounds when incorporated to obtain active films and their impact on the properties of polymeric matrices. Finally, the main factors affecting the effective action of active films in food substrates are also analyzed.

2 | BIODEGRADABLE POLYMERS FOR FOOD PACKAGING APPLICATIONS

The development of biobased polymers as a means of substituting petroleum-based synthetic plastics has been widely studied given the nondegradable and non-renewable nature of traditional plastics (DeGruson, 2016). So-called bioplastics are polymeric materials from renewable sources and/or are biodegradable or compostable (Zhong et al., 2020). Biodegradation is a natural

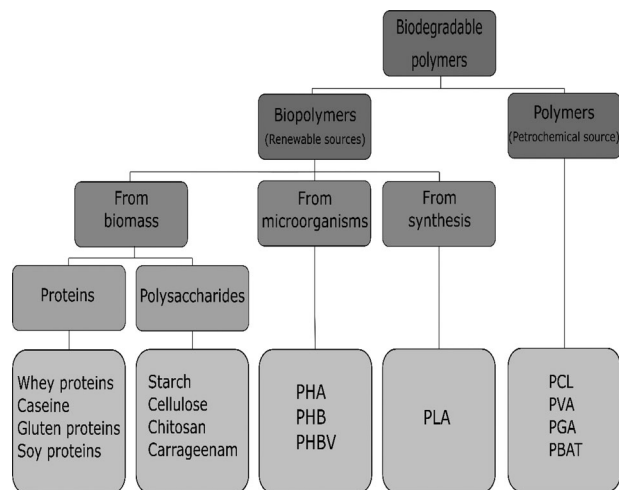


FIGURE 1 Classification of biodegradable polymers based on the source from which they are obtained. Adapted from Zhong et al. (2020)

decomposition process involving enzymatic processes triggered by microorganisms (Vert et al., 2012). Physical factors, such as sunlight, temperature, or moisture, can also intervene to turn certain polymers into viable substrates for microorganisms (Hernández-García et al., 2021a). Composting is a degradation process implying the hydrolysis of organic fractions (Wei et al., 2017) and involving thermophilic bacteria. In the initial stages of degradation, a temperature rise occurs due to the production of small molecules, such as sugars or amino acids, by mesophilic bacteria. Then, thermophilic bacteria reduce larger compounds (fats, cellulose, lignin, etc.) to small molecules that can be assimilated and metabolized by microorganisms. As the temperature drops back, the mesophilic organisms recolonize and degrade the metabolic residues producing water and CO₂ (Rastogi et al., 2020). Polylactic acid is an example of a polymer that degrades effectively under composting conditions.

Biopolymer is the term used for polymers originating from living organisms (Vert et al., 2012). Although most biopolymers are biodegradable, this is not the case for naturally sourced PET. Additionally, not all biodegradable polymers are bioderived (DeGruson, 2016), and some (such as polycaprolactone [PCL] or polyvinylalcohol) come from petrochemical sources. Figure 1 shows that biodegradable polymers can be classified according to their source, primarily either renewable or petrochemical, and secondarily according to the renewable source used. The most common natural source for bioplastic materials is biomass that is rich in polysaccharides (such as starch, cellulose, pectin, or chitosan) and proteins (gelatin, casein, whey protein, or soy protein) (Cheng et al., 2015). Bioplastics can also be synthesized from bioderived sources, such as

PLA (Vinod et al., 2020), or biosynthesized by bacteria (such as poly-hydroxy-alkanoates). These bioplastics still present some problems that hinder their practical application, such as unsatisfactory mechanical performance (brittleness, insufficient elongation, etc.) or deficient barrier properties in comparison to petroleum-based plastics. Polysaccharides tend to have low oxygen permeability, but given their hydrophilic nature, they offer poor resistance to water vapor. In contrast, polyesters such as PLA are very hydrophobic, with a higher water vapor barrier capacity, while being more permeable to oxygen and other gases (Requena et al., 2018). Table 1 summarizes recently reported data on the functional properties of some biopolymers frequently studied for food packaging. Both proteins and polysaccharides present good barrier properties to oxygen, but given their hydrophilic nature, they provide films with a poor barrier to water vapor.

Different promising strategies have been proposed to overcome these issues. The combination of two or more bioplastics with complementary barrier properties has been tested using two approaches: polymer blending and multilayer assemblies. Blending is usually performed by melt blending to obtain a mixed polymeric matrix. This technique has been used to add hydrophobic compounds or polymers to hydrophilic matrices, such as starch (Acosta et al., 2015; Ortega-Toro et al., 2015). However, the different polymer polarities and lack of chemical affinity could lead to phase separation and heterogeneous matrices, as observed in polycaprolactone and starch blends (Ortega-Toro et al., 2015b). On the other hand, multilayer materials can be obtained with fewer compatibility problems than polymer blending (Muller et al., 2017a). These materials can be assembled by thermocompression (Requena et al., 2018), coextrusion (Y. Zhu et al., 2016), casting (Uz & Altinkaya, 2011), or by electrospinning layers on already formed monolayers (Tampau et al., 2018).

In the following subsections, some of the most promising biodegradable polymers for food packaging applications are described.

2.1 | Polysaccharides

Starch has been widely studied, and it is one of the most naturally abundant polymers. It comes from multiple plant sources (such as cassava, corn, and potato) and is the least expensive biopolymer on the market (DeGruson, 2016). Its plastic properties can be improved by adding a plasticizer and other strategies. The blending and compatibilization of starch with other biodegradable polymers have been proven to enhance this low-cost material. For example, when starch is blended with other polysaccharides, such as xanthan or gellan gum, some mechanical limitations

TABLE 1 Properties of some biodegradable polymers for food packaging applications: Oxygen permeability (OP), water vapor permeability (WVP), elastic modulus (EM), tensile strength at break (TS), and percent elongation (E)

Polymer	Raw source	OP × 10 ¹⁴ (cm ³ /msPa)	WVP × 10 ¹² (g/msPa)	EM (MPa)	TS (MPa)	E (%)	Reference
Polysaccharides							
Starch	Cassava	6.37	2120	55	4.7	26	Menzel et al. (2019)
MC	Vegetal biomass	147	870	1604	66	15	Pastor et al. (2013)
HPMC	Vegetal biomass	1.06	1600	1327	71	14	Atarés et al. (2011)
Alginate	Brown seaweed	1.16	250	3200	80	5	Cofelice et al. (2019)
Chitosan	Crustacea	16.7	1200	2739	94	14	Pastor et al. (2013)
Proteins							
Sodium caseinate	Dairy	63.7	169	380	6	19	Fabra et al. (2011)
Gluten	Wheat	–	2.66	–	1.1	204	Hager et al. (2012)
Gelatin	Animal biomass	–	840	1970	61	11	Riahi et al. (2021)
Polyesters							
PLA	Lactic acid	1500	24	1599	49	3.5	Muller et al. (2017)
PHBV	Several bacteria	–	5.7	1688	37	3.4	Requena et al. (2018)
PCL	Petroleum based	–	32	304	18	1100	Ortega-Toro et al. (2015)
PBAT	Petroleum based	–	10	47	16	440	Cardoso et al. (2017)
Other							
PVA	Petroleum based	0.11	686	80	153	135	Andrade et al. (2020)

Abbreviations: MC, methylcellulose; PCL, polycaprolactone; PLA, polylactic acid; PVA, polyvinylalcohol.

can be improved (Hernández-García et al., 2021b). Blending starch with polyesters could also help overcome the main drawbacks of starch (poor water vapor permeability and low resilience), yielding more homogeneous materials with the help of compatibilizers (Zhong et al., 2020).

Cellulose is the most abundant organic compound on earth. Its derivatives, methylcellulose (MC), hydroxypropyl methylcellulose (HPMC), and carboxymethyl cellulose have shown excellent film-forming capacity, giving rise to films with excellent barrier capacities to hydrophobic compounds and good mechanical performance (Rubilar et al., 2015). In fact, biodegradable polymers consisting of starch and/or cellulose fibers or derivatives have growing possibilities of application (Zhong et al., 2020). Alginate can be obtained from different species of brown seaweeds at a low cost, and it has shown desirable film-forming properties (Cofelice et al., 2019). Chitin, which can be found in the exoskeleton of crustaceans and other biological materials, is the second most common naturally occurring biopolymer. Chitosan results from chitin deacetylation, and it has been proven to show good film-forming capacity as well as antimicrobial activity (Talón et al., 2017; Mohamed et al., 2020; Priyadarshi & Rhim, 2020).

2.2 | Proteins

Proteins, such as caseinate, whey protein, gluten, and gelatin, have been studied as potential food packaging materials. In general, due to their unique structure, protein films have better mechanical properties than polysaccharide films (Mohamed et al., 2020). However, they present poor mechanical strength, and their main drawback is their high-water vapor permeability.

2.3 | Synthetic and microorganism-produced biopolymers

Polyhydroxyalkanoates (PHAs) are a family of biopolyesters produced by many bacteria as intracellular storage carbon and an energy source against starvation (Chen et al., 2011). Although they present a high degree of crystallinity, they can be improved by blending with other polymers (Adeleye et al., 2020). Keskin et al. (2017) proposed several applications for PHAs, such as coated cardboard for milk or drink packaging. PLA is also a polyester that can originate from starch or other biomass polymers that are hydrolyzed to dextrose,

which is then transformed via fermentation into lactic acid, which finally is polymerized by different chemical routes (Madhavan Nampoothiri et al., 2010). PLA is a very versatile material exhibiting excellent barrier properties against water vapor. It has received great interest, as evidenced by the number of international patents it holds. In fact, it is currently considered to be the most promising compostable polymer (Evers et al., 2016; RameshKumar et al., 2020). Biodegradable polymers from petrochemical sources, such as PCL or polybutylene succinate, present ideal mechanical and thermal properties. PCL modifications have been demonstrated to overcome hydrophobicity and fast degradation problems because they are highly permeable to several agents, and PCL has been widely studied for use in drug delivery applications (Dash & Konkimalla, 2012).

3 | ACTIVE PROPERTIES OF Phenolic Acids

PAs are a subclass of phenolic compounds mainly encompassing hydroxybenzoic acids, hydroxyphenyl acetic acids, and hydroxycinnamic acids, which exhibit antioxidant and antimicrobial properties. They can be found in various plant sources, such as fruits, vegetables, spices, and grains. Both conventional and novel techniques have been used for PA extraction as reported by Al Jitan et al. (2018). These include Soxhlet extraction, liquid–liquid extraction, maceration, extraction assisted by microwave or ultrasound, accelerated solvent extraction, and supercritical fluid extraction. The selected method will be determined by the final application and the cost.

Phenolic acids are recognized compounds that exert an effect on biological systems, and they have received attention in pharmaceutical research because they seem to play a role in the prevention of several human diseases (Al Jitan et al., 2018). Rashmi and Negi (2020) reviewed the composition of PAs in a great variety of fruits and vegetables, and they also mapped the potential health benefits for possible nutraceutical applications for each species. They concluded that both hydroxybenzoic and hydroxycinnamic acids contribute to overall health improvement by virtue of their antioxidant, anti-inflammatory, antimicrobial, antimutagenic, hypoglycemic, and antiplatelet aggregating activities, as well as by prevention of stroke, cancer, and cardiovascular diseases.

The PA profile and content greatly affect the organoleptic quality of some food products, such as fruits and vegetables (Kumar & Goel, 2019) and have been correlated with the sensory acceptance of different wheat flours (Challacombe et al., 2012). In fact, these compounds can provide the food matrix with a variety of flavors, ranging

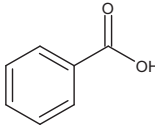
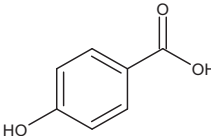
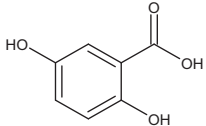
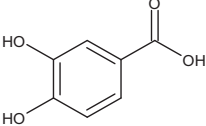
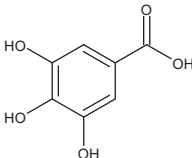
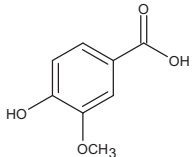
from sweet to bitter and astringent (Soto-Vaca et al., 2012) and colors (mainly their oxidized forms). Therefore, the use of these compounds as food additives or active packaging formulations should require specific studies about the sensory impact that these compounds have on the final product.

3.1 | Antioxidant properties of PAs

Not only PAs but also some of the products of PA metabolism retain strong antioxidant properties (Piazzon et al., 2012). The antioxidant activity of PAs is strongly affected by the acidic group (carboxyl, acetyl or ethylene) and the number and position of hydroxyl groups in the molecule (Rice-Evans et al., 1996). The electron-withdrawing properties of the carboxylate group in benzoic acids have a negative influence on the H-donating capacity of the hydroxy benzoates, whereas hydroxylated cinnamates or phenylacetates are more effective than benzoates. The insertion of an additional ethylene or methylene group between the phenyl ring and the carboxyl group in the hydroxycinnamic or hydroxyphenyl acetic acids mitigates the negative impact of the carboxylate group and promotes the antioxidant capacity of the molecules. This effect is more favorable on the reducing properties of the OH group in the hydroxycinnamic structures.

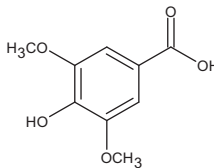
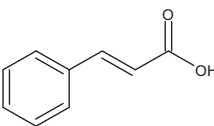
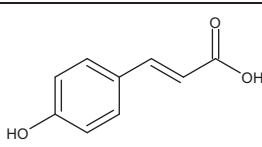
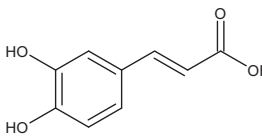
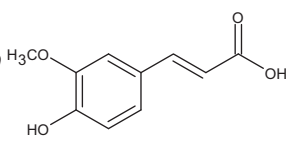
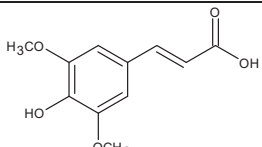
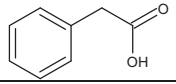
Table 2 gives the Trolox equivalent antioxidant activity (TEAC, mM), as reported by Rice-Evans et al. (1996) for the different PAs, allowing their different antioxidant activities to be ranked depending on the hydroxyl position in the aromatic ring relative to the carboxyl group. The monohydroxy benzoic acids in the ortho and para positions show no hydrogen-donating capacity, whereas in the meta position, they show a TEAC antioxidant activity of 0.84 mM. The ethylenic group in the hydroxycinnamic acids promotes the antioxidant properties of the OH group in any position of the aromatic ring compared with the equivalent OH position in PA. The equivalent m- and o-hydroxycinnamic acids have TEAC values closer to unity. The dihydroxybenzoic acid derivatives also show an antioxidant response dependent on the relative positions of the hydroxyl groups in the ring; 2,3-dihydroxy benzoic acid gives a TEAC value of 1.46 mM, which is slightly elevated compared to the 3,4 positions (TEAC 1.2 mM) and 2,5 positions (TEAC 1.1 mM). Thus, the proximity of the carboxyl group to the hydroxyl substituents affects their hydrogen donating capacity, with the m-position being the most effective. Therefore, the chemical structure of polyphenols, defining the availability of the phenolic hydrogens as radical scavengers, determines their antioxidant activity. However, the antioxidant activity of phenolic compounds also depends on the type of prooxidant and the

TABLE 2 Minimal inhibitory concentrations (MICs) of different phenolic acids for several microorganisms. The Trolox equivalent antioxidant activity (TEAC, mM) of phenolic acids was also included, as reported by Rice-Evans et al. (1996)

Acid	Structure	Microorganism	MIC (mg/g)	Reference
Hydroxybenzoic acids		<i>Escherichia coli</i>	1.00	Cueva et al. (2010)
		<i>Lactobacillus plantarum</i>	1.45	Sánchez-Maldonado et al. (2011)
		<i>Lactobacillus hammesii</i>	0.97	Sánchez-Maldonado et al. (2011)
		<i>Bacillus subtilis</i>	0.04	Sánchez-Maldonado et al. (2011)
	<p>p-hydroxybenzoic</p> <p>TEAC (mM): 0.08</p> 	<i>Escherichia coli</i>	0.12	Sánchez-Maldonado et al. (2011)
		<i>Escherichia coli</i>	0.34	Merkl et al. (2010)
		<i>Listeria monocytogenes</i>	0.69	Miyague et al. (2015)*
		<i>Listeria monocytogenes</i>	1.00	Cueva et al. (2010)
		<i>Listeria monocytogenes</i>	0.69	Merkl et al. (2010)
		<i>Lactobacillus plantarum</i>	1.57	Sánchez-Maldonado et al. (2011)
		<i>Lactobacillus hammesii</i>	1.12	Sánchez-Maldonado et al. (2011)
		<i>Bacillus subtilis</i>	0.13	Sánchez-Maldonado et al. (2011)
	<p>Gentistic</p> <p>TEAC (mM): 1.04</p> 	<i>Escherichia coli</i>	0.77	Merkl et al. (2010)
		<i>Listeria monocytogenes</i>	0.77	Merkl et al. (2010)
		<i>Bacillus cereus</i>	0.77	Merkl et al. (2010)
	<p>Protocatechuic</p> <p>TEAC (mM): 1.19</p> 	<i>Escherichia coli</i>	0.31	Sánchez-Maldonado et al. (2011)
		<i>Escherichia coli</i>	1.54	Merkl et al. (2010)
		<i>Listeria monocytogenes</i>	1.54	Miyague et al. (2015) *
		<i>Listeria monocytogenes</i>	0.77	Merkl et al. (2010)
		<i>Lactobacillus plantarum</i>	1.57	Sánchez-Maldonado et al. (2011)
		<i>Lactobacillus hammesii</i>	1.12	Sánchez-Maldonado et al. (2011)
		<i>Bacillus subtilis</i>	0.13	Sánchez-Maldonado et al. (2011)
	<p>Gallic</p> <p>TEAC (mM): 3.01</p> 	<i>Escherichia coli</i>	0.49	Sánchez-Maldonado et al. (2011)
		<i>Listeria monocytogenes</i>	1.70	Miyague et al. (2015)*
<i>Lactobacillus plantarum</i>		3.74	Sánchez-Maldonado et al. (2011)	
<i>Lactobacillus hammesii</i>		4.56	Sánchez-Maldonado et al. (2011)	
<i>Bacillus subtilis</i>		0.64	Sánchez-Maldonado et al. (2011)	
<p>Vanillic</p> <p>TEAC (mM): 1.43</p> 	<i>Escherichia coli</i>	1.00	Cueva et al. (2010)	
	<i>Escherichia coli</i>	1.64	Merkl et al. (2010)	
	<i>Listeria monocytogenes</i>	0.84	Miyague et al. (2015)*	
	<i>Listeria monocytogenes</i>	0.82	Merkl et al. (2010)	
	<i>Bacillus cereus</i>	0.82	Merkl et al. (2010)	

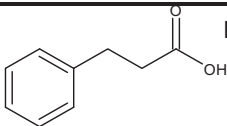
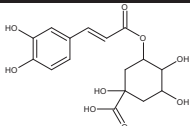
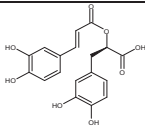
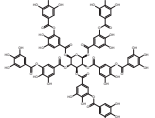
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TABLE 2 (Continued)

Acid	Structure	Microorganism	MIC (mg/g)	Reference	
Syringic TEAC (mM): 1.36		<i>Escherichia coli</i>	0.39	Sánchez-Maldonado et al. (2011)	
		<i>Listeria monocytogenes</i>	0.99	Miyague et al. (2015)*	
		<i>Lactobacillus plantarum</i>	1.75	Sánchez-Maldonado et al. (2011)	
		<i>Lactobacillus hammesii</i>	1.15	Sánchez-Maldonado et al. (2011)	
		<i>Bacillus subtilis</i>	0.26	Sánchez-Maldonado et al. (2011)	
Cinnamic		<i>Escherichia coli</i>	0.11	Sánchez-Maldonado et al. (2011)	
		<i>Listeria monocytogenes</i>	1.48	Miyague et al. (2015)*	
		<i>Lactobacillus plantarum</i>	0.79	Sánchez-Maldonado et al. (2011)	
		<i>Lactobacillus hammesii</i>	0.86	Sánchez-Maldonado et al. (2011)	
		<i>Bacillus subtilis</i>	0.07	Sánchez-Maldonado et al. (2011)	
p-Coumaric TEAC (mM): 2.22		<i>Escherichia coli</i>	0.12	Sánchez-Maldonado et al. (2011)	
		<i>Listeria monocytogenes</i>	0.82	Miyague et al. (2015)*	
		<i>Lactobacillus plantarum</i>	1.21	Sánchez-Maldonado et al. (2011)	
		<i>Lactobacillus hammesii</i>	1.04	Sánchez-Maldonado et al. (2011)	
		<i>Bacillus subtilis</i>	0.25	Sánchez-Maldonado et al. (2011)	
Caffeic TEAC (mM): 1.26		<i>Escherichia coli</i>	0.23	Sánchez-Maldonado et al. (2011)	
		<i>Escherichia coli</i>	0.25	Matejczyk et al. (2018)	
		<i>Escherichia coli</i>	1.80	Merkl et al. (2010)	
		<i>Listeria monocytogenes</i>	1.80	Merkl et al. (2010)	
		<i>Lactobacillus plantarum</i>	1.52	Sánchez-Maldonado et al. (2011)	
		<i>Lactobacillus hammesii</i>	0.63	Sánchez-Maldonado et al. (2011)	
		<i>Bacillus subtilis</i>	0.30	Sánchez-Maldonado et al. (2011)	
		<i>Bacillus cereus</i>	1.80	Merkl et al. (2010)	
Ferulic TEAC (mM): 1.90		<i>Escherichia coli</i>	0.16	Sánchez-Maldonado et al. (2011)	
		<i>Escherichia coli</i>	1.94	Merkl et al. (2010)	
		<i>Listeria monocytogenes</i>	0.97	Miyague et al. (2015)*	
		<i>Listeria monocytogenes</i>	1.94	Merkl et al. (2010)	
		<i>Lactobacillus plantarum</i>	1.68	Sánchez-Maldonado et al. (2011)	
		<i>Lactobacillus hammesii</i>	0.89	Sánchez-Maldonado et al. (2011)	
		<i>Bacillus subtilis</i>	0.38	Sánchez-Maldonado et al. (2011)	
		<i>Bacillus cereus</i>	1.94	Merkl et al. (2010)	
Sinapinic		<i>Listeria monocytogenes</i>	1.12	Miyague et al. (2015)*	
Phenylacetic		<i>Escherichia coli</i>	0.50	Cueva et al. (2010)	
		3-hydroxyphenylacetic TEAC (mM): 0.90	<i>Escherichia coli</i>	1.00	Cueva et al. (2010)
		3,4-dihydroxyphenylacetic TEAC (mM): 2.19	<i>Escherichia coli</i>	1.00	Cueva et al. (2010)

(Continues)

TABLE 2 (Continued)

	Acid	Structure	Microorganism	MIC (mg/g)	Reference
Phenylpropionic	Phenylpropionic		Escherichia coli	0.50	Cueva et al. (2010)
	3-hydroxyphenylpropionic		Escherichia coli	1.00	Cueva et al. (2010)
	3,4-dihydroxyphenylpropionic		Escherichia coli	1.00	Cueva et al. (2010)
Other phenolic acids	Chlorogenic		Escherichia coli	1.00	Cetin-Karaca & Newman (2015)
	Rosmarinic		Escherichia coli	0.25	Matejczyk et al. (2018)
	Tannic		Escherichia coli Listeria monocytogenes	0.025 0.025	de Almeida Roger et al. (2018) de Almeida Roger et al. (2018)

*Value at pH 6.

antioxidant to prooxidant ratio; under certain conditions, certain antioxidants, including PAs, can behave as prooxidants (Carocho & Ferreira, 2013). Both factors are important for the efficiency of phenolics in the inhibition of catalyzed oxidations. Therefore, when a particular phenolic compound is selected for an application, the type and content of different pro-oxidative agents should be known, since different reactions are involved in interactions between pro-oxidants and antioxidants.

3.2 | Antimicrobial properties of PAs

The capacity of PAs to inhibit bacterial growth is due to their pro-oxidative properties and their ability to alter the cell's superficial charge and hydrophobicity, causing fissures and cytoplasmic deposition (Maddox et al., 2010). Previous studies (Cueva et al., 2010) demonstrated that Gram-positive bacteria are more susceptible to the action of PAs than Gram-negative bacteria. This activity can be influenced by the molecular structure of the PA, specifically the type and position of the substituents in the aromatic ring and the length of the lateral chain. This structural effect was widely studied by Sánchez-Maldonado et al. (2011) working on lactic acid bacteria with different conclusions for hydroxycinnamic and hydroxybenzoic acids. The antibacterial activity of hydroxybenzoic acids decreased as the number of hydroxyl groups increased, which promoted the hydrophilic nature of the

compounds and highly increased as the hydroxyl groups were substituted by methoxy groups, thus boosting the lipophilic character of the molecule. However, the activity of hydroxycinnamic acids was not significantly affected by the aromatic ring substitutes since it was heavily dependent on the conjugated double bond on the side chain. This insight could facilitate the selection of PAs for food antimicrobial applications.

Table 2 shows the values of the MIC against different bacteria of different PAs, as reported by several authors. Coumaric, ferulic, and syringic acids exhibited inhibition capacity against *Listeria monocytogenes* (Miyague et al., 2015), with this activity being higher at lower pH levels when PAs are not ionized and can easily cross the plasma membrane; once they enter the cytoplasm, they can disrupt many metabolic pathways. These authors also tested the efficacy of combinations of some EO compounds and PAs against *L. monocytogenes*, finding several synergistic effects at pH 5, which points to the potential use of these compound combinations in acidic foods to control bacterial growth. Malheiro et al. (2018) reported a significant growth inhibition of planktonic and sessile bacteria for cinnamic acid, cinnamaldehyde, and their derivatives. Merkl et al. (2010) studied the antimicrobial and antioxidant capacities of several alkyl esters of PAs and reported enhanced antioxidant and antimicrobial activity of the esters of protocatechuic and caffeic acids compared to the respective acids, while the antimicrobial power of these derivatives increased as the alkyl chain became longer.

Based on the aforementioned studies and their potential health benefits, PAs appear to be promising compounds for the purposes of obtaining active materials for food packaging applications with a double-action, antioxidant, and antimicrobial capacity, which confers great potential for food preservation and shelf-life extension. Nevertheless, their incorporation into packaging films may provoke changes in the functional properties of the materials, and their release from this would be required to ensure an effective role in food preservation. The following sections discuss different studies where PAs, or plant extracts potentially rich in these compounds, have been incorporated into different polymer matrices, analyzing their effect on the barrier and tensile properties and antimicrobial or antioxidant properties of the materials.

4 | FUNCTIONAL AND ACTIVE PROPERTIES OF BIODEGRADABLE FILMS CONTAINING PHENOLIC ACIDS/PLANT EXTRACTS

As discussed above, hydrophilic biopolymer-based films and coatings exhibit water sensitivity, along with poor mechanical and barrier properties, which limits their practical applications. Phenolic compounds, particularly PAs, have been tested as cross-linkers to improve the properties of some biopolymer films, such as those that are protein-based, involving the formation of both covalent and noncovalent bonding (Zhang et al., 2010). Phenolic acids are present in many natural foods, and due to their antioxidant capacity, among other properties, these compounds provide food with health benefits and oxidative stability (Soto-Vaca et al., 2012). The following sections discuss the effect of PA incorporation on the functional or active properties of biodegradable materials intended for food packaging applications.

4.1 | Functional properties

Table 3 summarizes recent studies in which PAs or plant extracts have been incorporated into biodegradable films based on different materials, analyzing their mechanical and barrier properties.

4.1.1 | Mechanical properties

The mechanical properties of film-forming materials play an important role in preserving the physical integrity of packaged foods, and some values are required to

ensure food integrity, avoiding discontinuities (Azeredo & Waldron, 2016).

Cross-linking is frequently used to improve the performance and resistance of biopolymeric films (Choi et al., 2018). In this reaction, bonds between a cross-linking agent and the polymeric chains are created (Hager et al., 2012). Chemical cross-linking is attained if covalent bonds are predominant, while physical cross-linking refers to hydrogen, ionic, and other noncovalent interactions. Given their high number of functional groups, these techniques have been commonly utilized in protein films (Azeredo & Waldron, 2016). Cross-linking results in a reduction in molecular mobility and free volume in the system, which, in turn, gives rise to improved barrier properties, an increased glass transition temperature, improved resistance to light and heat, and a general solubility reduction while making the structure stiffer (Azeredo & Waldron, 2016). Cross-linking may also retard the biodegradation process in polysaccharides and proteins. The main drawback of cross-linking for food packaging purposes is that the most commonly used agents, such as linear short-chain aldehydes, have been reported to be toxic (Makishi et al., 2013). Genipin and transglutaminase have been recognized as safe cross-linkers, but they are too expensive for industrial applications. Therefore, there is a demand for new low-cost, safe cross-linkers (Picchio et al., 2018).

Phenolic compounds have been reported to act as cross-linking agents in different polymeric matrices, which can benefit the properties of the material (Azeredo & Waldron, 2016). The oxidation of phenolic compounds yields quinones, which can react with the side chains of proteins, forming new covalent bonds (C–N or C–S) and leading to hydrogen bonding (Makishi et al., 2013). J. Liu et al. (2017) suggested similar mechanisms for this cross-linking effect on chitosan grafted with PAs. Strong intermolecular connections between chains reduce the free space in the polymeric matrix, resulting in a denser, stiffer, and more tightly packed structure with reduced molecular mobility (Makishi et al., 2013). Nevertheless, some studies describe PAs as film plasticizers rather than cross-linking agents by forming hydrogen bonds with the polymer matrix, replacing polymer–polymer interactions and increasing the free volume of the matrix, hence reducing tensile strength (Azeredo & Waldron, 2016). Hager et al. (2012) reported both effects of different PAs on the gluten matrix: gallic acid affected the mechanical properties acting as a plasticizer, while tannic acid exhibited cross-linking behavior. Choi et al. (2018) found that for phenolic oxidized substances, the cross-linking effect predominated at low concentrations, whereas the plasticizing effect predominated at high concentrations. Arcan and Yemencioğlu (2011) studied the mechanical properties of zein films with several incorporated PAs and found that

TABLE 3 Studies into the effect of the incorporation of phenolic acids/plant extracts on the functional properties (EM, elastic modulus; TS, tensile strength at break; E, elongation at break; WVP, water vapor permeability; OP, oxygen permeability) of several biodegradable polymeric matrices

Material	Active compound	Highlights	Reference
Alginate	Grape seed and green tea extracts	WVP improved with the highest concentrations of extracts.	Fabra et al. (2018)
Alginate	Tannic acid	Plastic behavior was improved, reduced surface hydrophilic character. OP and WVP were increased.	Kaczmarek (2020)
Casein	Tannic acid	TS increased while E decreased in relation to the acid concentration, WVP decreased greatly at low concentrations.	Picchio et al. (2018)
Cassava starch	Rosemary extract	TB decreased in every sample, WVP greatly increased at high extract concentrations.	Piñeros-Hernandez et al. (2017)
Chitosan	Propolis extract	E, TS, and OP increased while WVP decreased.	Siripatrawan and Vitchayakitti (2016)
Chitosan	Gallic, ferulic, p-coumaric, salicylic, and vanillic acids	All acids reduced E, TS, and water solubility. Ferulic and gallic acids gave rise to the best properties.	Liu et al. (2021)
Chitosan and chitosan-corn starch	Murta leaf extract	Extract created discontinuity in films and reduced E.	Silva-Weiss et al. (2013)
Chitosan, gelatin and MC	Tannic acid	E increased in chitosan and MC but decreased in gelatin. OP decreased in chitosan and gelatin. WVP decreased in all formulations.	Halim et al. (2018)
Chitosan-alginate	Ferulic acid	E decreased in the mixed material, WVP also decreased in every sample.	Li et al. (2019)
Chitosan-PVA	Mint and pomegranate peel extracts	Extracts increased TS but did not alter WVP or OP.	Kanatt et al. (2012)
Fish myofibrillar protein	Caffeic, ferulic, and tannic acids	EM and TS increased, while E decreased in every acid concentration.	Prodpran et al. (2012)
Bovine gelatin	Rosmarinic acid	Reduced TS, EM, and WVP while E increased.	Ge et al. (2018)
Gellan gum	Coffee parchment waste	E and TS decreased.	Mirón-Mérida et al. (2019)
Gluten	Gallic and tannic acids	Gallic acid increased E and WVP, while decreasing TS. The opposite was observed for tannic acid.	Hager et al. (2012)
PLA-starch-PBAT blend	Ferulic acid or ferulic acid-coupled chitosan	WVP increased but OP decreased, E increased for the mixed material but decreased for chitosan.	Woranuch et al. (2015)
PLA-PBAT blend	Ferulic acid	TS and thermal stability increased and internal transmittance decreased by the acid incorporation.	Sharma et al. (2020)
PVA	Cinnamic and ferulic acids	Films containing ferulic acid were mechanically stiffer and had enhanced barrier properties	Andrade et al. (2021)
Potato starch	Sunflower hull extracts	EM increased, while E, WVP, and OP decreased	Menzel et al. (2019)
Soy protein	Ferulic, caffeic, and gallic acids	All the acids increased E and TS while reducing WVP.	Insaward et al. (2015)
Turmeric and gelatin	Tannic and caffeic acids	No significant differences with unoxidized forms. With oxidized acids, WVP decreased, and E increased.	Choi et al. (2018)
Zein	Gallic, ferulic, and hydroxybenzoic acids	All the acids increased E while reducing EM and TS. Gallic prevented the films from swelling.	Arcan and Yemenicioğlu (2011)
Zein	Gallic, vanillic, and cinnamic acids	Plastic behavior was promoted by all the acids and concentrations.	Alkan and Yemenicioğlu (2016)
Zein/chitosan	Ferulic and gallic acids	Both acids increased E and TS while reducing WVP.	Cheng et al. (2015)

Abbreviations: MC, methylcellulose; PLA, polylactic acid; PVA, polyvinylalcohol.

these had a plasticizing effect, eliminating the brittleness of the films and increasing their elongation capacity. This effect was explained by the binding of phenolic compounds to the zein protein surface, leading to an increased free volume in the matrix. Sharma et al. (2020) also found a cross-linking effect in PLA/PBAT (poly(butylene adipate co-terephthalate)) blend films obtained by casting when ferulic acid was incorporated into the polyester matrix at 10% w/w, increasing the film tensile strength and thermal stability. Nevertheless, this effect was not so clearly observed at lower concentrations of ferulic acid.

4.1.2 | Barrier properties

The barrier capacity of films is mainly affected by the film-forming material and the additives, as well as by the film preparation process (Cheng et al., 2015). Phenolic acid incorporation tends to reduce the water vapor permeability (WVP) of some biodegradable films, and this trend is predominant at low concentrations, where the hydrophobic nature of phenolic compounds hinders water diffusion through the matrix (Cheng et al., 2015). Moreover, the possible cross-linking that could rearrange the matrix occupying the empty molecular space could also hinder the migration of both water and oxygen molecules (Choi et al., 2018). At high concentrations, PAs could promote a heterogeneous arrangement, creating nonbound phenolic fractions and oligomers (Zhang et al., 2010), which could ultimately permit the easy passage of water molecules, as observed by Piñeros-Hernandez et al. (2017). Apart from the concentration effect, Choi et al. (2018) reported the specific effect of each PA by comparing caffeic and tannic acids at the same concentration. Tannic acid reduced WVP to a greater extent, which was attributed to its high number of hydroxyl groups. In most studies, oxygen migration is clearly reduced by PA incorporation. As mentioned above, this could stem from the cross-linking rearrangement together with the antioxidant effect of phenolic compounds that could promote an oxygen scavenging effect (Bonilla et al., 2012).

4.1.3 | Optical properties

Optical properties that might influence the characteristics of a film's appearance, such as color or transparency, are also important for practical applications. Cheng et al. (2015) reported a significant reduction in lightness (L^*) brought about by the addition of PAs to zein and chitosan films, as well as hue or chrome changes in the material. Azeredo and Waldron (2016) also concluded that a general

disadvantage of the incorporation of phenolic compounds into films is the promotion of color changes. The darkening effect, which was dependent on the PA added, was partly attributed to the oxidation of phenolic compounds yielding quinones.

4.2 | Active properties

The effectiveness of an active packaging material depends on its capacity to preserve food quality and safety. Table 4 summarizes recent studies on the antimicrobial and antioxidant properties of biodegradable films, mainly based on proteins or polysaccharides, with incorporated PAs or plant extracts rich in PAs. The effectiveness of the film at controlling bacterial growth has predominantly been studied using in vitro tests in inoculated culture media, whereas few studies analyze the antimicrobial effects in real foods. Likewise, several methods have been used to test the antioxidant activity of the materials, such as DPPH radical inhibition (Menzel et al., 2019), ABTS radical inhibition (Fabra et al., 2018), or ferric antioxidant power assay (FRAP) (Salgado et al., 2012). In most cases, films loaded with PAs exhibited the expected antimicrobial or antioxidant capacities with differing intensities, depending on the polymer matrix or compound concentration. Azeredo and Waldron (2016) discussed the mechanism of the antioxidant activity caused by PAs. The antioxidant power of PAs and their potential to reduce the oxygen permeability of the material due to cross-linking may act together to reduce oxidation reactions in food systems.

In most studies on the active properties of materials with phenolics, biopolymers from biomass (proteins and polysaccharides) prepared by solvent casting were used. However, thermal treatments for film production, which are normally used on an industrial scale, do not seem to significantly reduce their antioxidant activity. Menzel et al. (2019) incorporated sunflower hull extract into thermoplastic starch and found antioxidant activity in films obtained by melt-blending and compression molding. Woranuch et al. (2015) used the extrusion method to incorporate pure ferulic acid and ferulic acid coupled to chitosan by means of its bonding to the amino group into a biodegradable material composed of PLA, thermoplastic starch, and PBAT. The radical scavenging activity of materials with incorporated ferulic acid coupled to chitosan was almost three times higher than those with pure ferulic acid. Quiles-Carrillo et al. (2019) incorporated gallic acid into PLA by using electrospinning. The antioxidant nanofibers obtained were able to release the active compound directly or through a thin layer of thermally processed PLA.

TABLE 4 Studies into the incorporation of phenolic acids/plant extracts into biodegradable polymeric matrices and their effect on the film's active properties (antioxidant or antimicrobial)

Material	Active compound	Highlights	Reference
Alginate	Grapeseed or green tea extracts	Both extracts impaired the antiviral (against murine norovirus and hepatitis A virus) and antioxidant (TEAC) activities of the films.	Fabra et al. (2018)
Alginate	Tannic acid	Films exhibited antioxidant activity as a function of the concentration of tannic acid.	Kaczmarek (2020)
Bovine gelatin	Rosmarinic acid	Long-term antibacterial activity was observed against <i>E. coli</i> and <i>S. aureus</i> . The ABTS method showed effective antioxidant activity.	Ge et al. (2018)
Cassava starch	Rosemary extract	DPPH scavenging activity increased as did the polyphenol content of the films.	Piñeros-Hernandez et al. (2017)
Chitosan	Propolis extract	Enhanced antimicrobial activity against <i>E. coli</i> , <i>S. aureus</i> , <i>Pseudomonas aeruginosa</i> , and <i>Salmonella enteritidis</i> . Antioxidant capacity (DPPH) greatly increased.	Siripatrawan and Vitchayakitti (2016)
Chitosan	Gallic, ferulic, p-coumaric, salicylic, and vanillic acids	DPPH scavenging activity was significantly increased in all formulations except with salicylic acid. Antibacterial activity was enhanced by all acids. Ferulic and p-coumaric formulations extended shrimp shelf life.	Liu et al. (2021)
Chitosan, gelatin or MC	Tannic acid	Growth inhibition of <i>E. coli</i> and <i>S. aureus</i> was reported for all the formulations containing tannic acid.	Halim et al. (2018)
Chitosan-PVA	Mint or pomegranate peel extracts	Films exhibited antibacterial activity against <i>S. aureus</i> and <i>B. cereus</i> but did not inhibit the growth of Gram-negative bacteria, such as <i>E. coli</i> or <i>P. fluorescens</i> . Extracts conferred antioxidant properties on the films as determined by the DPPH method.	Kanatt et al. (2012)
Corn starch	Tannic acid	Films inhibited the growth of <i>E. coli</i> and <i>L. monocytogenes</i> . Tannic acid solutions exhibited antioxidant activity, protecting vegetable oils from air oxidation (Rancimat method). Tannic acid was reported to gain activity after thermal processing.	Pyla et al. (2010)
Gellan gum	Coffee parchment waste extract	Gallic, chlorogenic, p-coumaric, and synapic acids were identified in the extract. Films exhibited antifungal activity against <i>Fusarium verticillioides</i> , <i>Fusarium</i> sp., and <i>Colletotrichum gloeosporioides</i> .	Mirón-Mérida et al. (2019)
PLA (electrospun)	Gallic acid	DPPH assay showed the high antioxidant capacity of electrospun mats. The release of the acid through a multilayer assembly was demonstrated in the saline medium.	Quiles-Carrillo et al. (2019)
PLA-starch-PBAT blend.	FA or ferulic acid-coupled chitosan	DPPH and reducing power assay showed that FA-coupled chitosan was a significantly stronger antioxidant agent than FA. The peroxide value of potato chips stored in the films containing FA-coupled chitosan was reduced by approximately 32%.	Woranuch et al. (2015)
PLA-PBAT blend	Ferulic acid	Films effectively inhibited <i>E. coli</i> and <i>L. monocytogenes</i> growth in liquid media, as a function of ferulic acid concentration.	Sharma et al. (2020)
Potato starch	Sunflower hull extracts	Chlorogenic acid was identified by the DPPH method as the main active compound with demonstrated antiradical activity.	Menzel et al. (2019)
Sodium alginate	Tannic acid	The antioxidant activity increased with the increasing content of tannic acid	Kaczmarek (2020)
Sunflower protein concentrate	Naturally, present phenolic compounds	Films exhibited considerable antioxidant capacity (ABTS, FRAP and PCL assays) but no antimicrobial activity against 26 microbial strains.	Salgado et al. (2012)

(Continues)

TABLE 4 (Continued)

Material	Active compound	Highlights	Reference
Tuna or bovine gelatin	Oregano or rosemary extracts	Rosmarinic acid was the most abundant phenolic compound of the extracts. Both extracts promoted the antioxidant activity (FRAP and ABTS) of the gelatin matrices. In the same extract concentration, bovine gelatin was more active than tuna gelatin.	Gómez-Estaca et al. (2009)
Turmeric-gelatin	Oxidized green tea extract, tannic, or caffeic acids	Turmeric-gelatin films exhibited DPPH inhibition capacity, which was not improved by the incorporation of phenolics. When applied to ground pork meat, all the films were effective at reducing TBA values.	Choi et al. (2018)
Zein	Gallic acid	Films exhibited antioxidant capacity (ABTS) and inhibited the growth of <i>Listeria monocytogenes</i> and <i>Campylobacter jejuni</i> .	Arcan and Yemenicioğlu (2011)
Zein	Gallic, vanillic, or cinnamic acids	Films containing PA inhibited plant pathogens, such as <i>Erwinia amylova</i> , <i>Erwinia cartavora</i> , <i>Xanthomonas vesicatoria</i> , and <i>Pseudomonas syringae</i> . Gallic acid exhibited the highest activity.	Alkan and Yemenicioğlu (2016)
Zein-chitosan	Ferulic or gallic acids	Both acids in the composite films enhanced the growth inhibition of <i>E. coli</i> and <i>S. aureus</i> , while also conferring antioxidant activity (DPPH and ABTS).	Cheng et al. (2015)

Abbreviations: FA, Ferulic acid; MC, methylcellulose; PLA, polylactic acid; PVA, polyvinylalcohol.

4.2.1 | Antioxidant properties

Arcan and Yemenicioğlu (2011) studied the incorporation of gallic acid into zein films and obtained films with a high ABTS radical inhibition, which released 88% of the incorporated acid. This high release rate, associated with the high antioxidant capacity, was attributed to the relaxation of the hydrophilic matrix in contact with water. Piñeros-Hernandez et al. (2017) studied the antioxidant activity of starch incorporated with rosemary extract, which exhibited high release rates of active compounds in water, but only a very small quantity of phenolics was delivered when using ethanol as a fatty simulatant. Phenolic acids can also exert their antioxidant capacity through their oxidized form, as reported by Choi et al. (2018) in the case of turmeric-gelatin films loaded with oxidized extracts. While the DPPH radical scavenging activity of turmeric-gelatin films was not significantly affected by any component, the films with oxidized extracts notably limited the oxidation of stored pork meat. Nevertheless, a good antioxidant capacity is not necessarily correlated with good antimicrobial activity. Salgado et al. (2012) developed films with sunflower protein concentrate, which presented good antioxidant capacity that was attributed to the main PAs found in the concentrate (chlorogenic and caffeic acids). However, antimicrobial assays showed no growth inhibition against any of the 21 different strains tested, which was attributed to the high pH value (approximately 11) in the film-forming dispersions that

promoted the dissociation of acids, thus reducing their antimicrobial activity.

4.2.2 | Antimicrobial activity

The antimicrobial activity of potentially active films has been estimated by different methods; qualitative methods offer an initial approach to discover the potential activity, while quantitative methods should be carried out for final conclusions. Pyla et al. (2010) used disc diffusion in agar medium and viable cell counts to test the antimicrobial activity against *Escherichia coli* and *L. monocytogenes* of starch-based films with tannic acid submitted or not to thermal treatment. The zone of inhibition successfully increased with tannic acid concentration for both treatments. However, cell counts for untreated tannic acid did not significantly inhibit *L. monocytogenes* in TSB media. Likewise, Fabra et al. (2018) proved the antiviral properties of alginate films carrying grape seed or green tea extracts against murine norovirus and hepatitis A virus. Although some antiviral activity was exerted by the films with extracts, it was significantly lower than in the pure extracts alone, which suggests that a part of the active compounds was retained in the films by bonding with the alginate matrix. Cheng et al. (2015) incorporated gallic and ferulic acids into zein-chitosan composite films and observed growth inhibition of *E. coli* and *Staphylococcus aureus* for films with both acids. The greatest

antibacterial effect was obtained in the case of gallic acid, which contrasts with previous studies that reported lower MIC values for ferulic acid than for gallic acid against *E. coli* (Sánchez-Maldonado et al., 2011). This was explained by the interactions of chitosan and ferulic in the film matrix that limit its release and effective action against bacteria. Ge et al. (2018) observed antibacterial activity against *E. coli* and *S. aureus* for gelatin films with rosmarinic acid (with very low MIC values). They described morphological changes associated with the destruction of the bacterial cell membrane after being in contact with the films using SEM observations.

4.2.3 | Sensory impact

Few studies have analyzed the sensory impact of PAs incorporated into packaging materials on food matrices in contact. Choi et al. (2018) studied the organoleptic acceptance of pork meat packaged with turmeric–gelatin films loaded with oxidized tannic and caffeic acid, and no negative effect on the product sensory acceptance was observed, while lipid oxidation was prevented. W. Liu et al. (2021) observed an improved sensory score in shrimp (*Penaeus vannamei*) stored in chitosan films with ferulic and p-coumaric acids in comparison with those in contact with films of chitosan alone. While limited, these studies showed promising results for active food packaging with PAs to enhance food shelf life without altering organoleptic properties.

Ferulic, gallic, and tannic acids are among the most widely studied PAs with regard to the development of active packaging applications. These and other promising compounds, such as cinnamic or rosmarinic acids, have yet to be further explored for antimicrobial packaging applications in food matrices. However, the antimicrobial effectiveness of potentially active films is dependent not only on the effectiveness of the incorporated active compound but also on other factors affecting the release kinetics of the active agent from the food packaging material and its final partition between packaging and food. The following section analyzes these factors to understand the different activities found for the determined compounds, depending on the polymeric matrix and food substrate.

5 | FACTORS AFFECTING THE ANTIMICROBIAL EFFICIENCY OF BIODEGRADABLE ACTIVE MATERIALS IN CONTACT WITH FOOD PRODUCTS

Target microorganism(s) must be identified prior to adequate selection of the active ingredient for the purposes of

designing effective antimicrobial films for food packaging. Moreover, polymers must be selected according to their functional properties and the specific requirements of the food product. The incorporation of an antimicrobial agent into the polymeric material might modify its functional properties; therefore, these properties must be reanalyzed to assess the true effectivity of the food packaging system. As discussed above, some antimicrobial additives, such as several PAs, can act as plasticizers or cross-linkers, modifying the tensile properties of the films. However, in general, the film strength has been observed to decrease while the concentration of such active substances increases (Choi et al., 2018). Interactions of the active compounds and the polymer through hydrogen bonds, hydrophobic or electrostatic forces can influence the physical properties of the material linked to its functionality (F. Zhu, 2021). Likewise, the presence of antimicrobial compounds in the material may affect its biodegradation behavior since the release of these compounds could alter the microbial population responsible for this phenomenon, while these compounds modify the sensitivity of the polymer matrix to the physical degradation processes through changes in the matrix cohesion forces or wetting capacity (Hernández-García et al., 2021a).

5.1 | Factors determining the release and efficiency of the antimicrobial agent

Regarding the antimicrobial effectiveness of the material containing antimicrobial agents for food preservation purposes, Figure 2 shows different factors that can affect the release of the active compounds from the polymeric matrix and their migration to the food product surface, which will in turn affect their antimicrobial activity. The compositions of both the polymeric matrix and the foodstuff, as well as the interactions between components, determine the migration mechanisms between both phases (packaging material and food) in contact, resulting from the differences in the chemical potential of each component in the respective phase. Thus, both the release kinetics and the amount of antimicrobial at equilibrium released into the food system determine its effective action. Moreover, the food composition also affects the effectiveness of the antimicrobial agent. The foodstuff composition impacts microbial growth, and the food components can exert different/opposite functions, thus affecting antimicrobial action. In fact, some components are adequate nutrients for the microbial population, enhancing its vitality and resistance, while some of these can act as sequestrants on the active compound due to specific interactions. Requena et al. (2019a) found that the microbial growth inhibition of EO compounds, such as carvacrol and eugenol

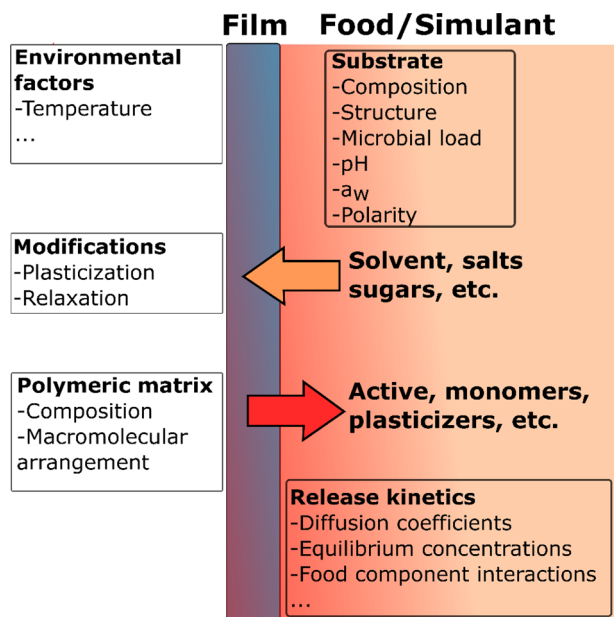


FIGURE 2 Mass transfer phenomena between film packaging and food systems, showing the factors influencing the antimicrobial effectiveness of active films

incorporated into poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) matrices, was different in several food matrices, such as cheese, chicken breast, and fresh-cut melon or pumpkin. Food components can modify the interactions of antimicrobial compounds and pathogens; certain lipids and proteins are known to exert a protective action on bacterial targets (Juneja et al., 2012). It has also been suggested that, given the lipophilic nature of many antimicrobial compounds, they tend to dissolve in the lipid phase or bind to other components of the food and become less available to bacteria in the aqueous phase, hence requiring higher concentrations to exert their antimicrobial activity (Prakash et al., 2018). Likewise, phenolic compounds can react with free radicals stemming from fat oxidation, which could also reduce their effectiveness (Pyla et al., 2010). Additionally, some other characteristics of the food substrate, such as water activity and pH, can alter the MIC for a given microorganism—antimicrobial combination (Juneja et al., 2012; Miyague et al., 2015).

The active compound concentration released during storage is an essential factor in ensuring antimicrobial efficiency and food safety (Requena et al., 2019a). Therefore, the antimicrobial efficiency of films carrying active compounds depends not only on the nature of the additive but also on the capacity of the film to release it into the food substrate at an adequate rate, finally maintaining an appropriate concentration at equilibrium. This, in turn, depends on the active compound interactions with

the polymer matrix and its solubility in the food system (Requena et al., 2017). The chemical affinity of the active substance with both phases (packaging material and food system) will greatly affect the equilibrium concentrations reached in both phases (partition coefficient). In some cases, the entire antimicrobial compound is rapidly released into the food matrix, and its effect ceases once it is depleted. The minimal inhibitory concentration of the compound for a target microorganism must be locally reached at the contaminated point of the food system.

Some chemical species also migrate from the food substrate toward the polymeric matrix. The release kinetics of the active compound are, hence, affected by three mechanisms: (1) the diffusion of food components, such as water or fat, toward the polymeric matrix, (2) the relaxation of the macromolecular structure due to diffusion/plasticization, and (3) the diffusion of the active compound through the relaxed polymeric matrix until reaching thermodynamic equilibrium between film and food (Requena et al., 2017). Matrix plasticization improves molecular mobility, so the rate of all the diffusional processes can markedly increase. Consequently, the ability of the polymeric matrix to be plasticized by migrated food components (such as water or oil) can greatly accelerate the diffusion process.

The MIC value of target microorganisms must be reached in the food matrix in contact with the active film to effectively prevent antimicrobial growth. This state must be reached at the right time to avoid the initial proliferation that could augment the resistance of the target microorganism. Nevertheless, the food matrix composition, pH, water activity, and other factors can change the MIC value for a specific microorganism and active compound. pH plays a particularly important role in the effectivity of ionizable compounds in aqueous media, such as PAs, since it influences the proportion of dissociated and protonated forms with different activities. Miyague et al. (2015) demonstrated that the antimicrobial activity of PAs is higher at a pH below their pKa when the protonated form predominates.

Environmental factors, such as temperature, can affect the release rate and antimicrobial effectiveness of active compounds. Provided that the antimicrobial additive is not thermosensitive, a high temperature can potentially increase the release rate and improve its antimicrobial effect to a greater extent than microbial growth. However, this balance could ultimately lead to a counterproductive result. The temperature has a great impact on the molecular mobility of the polymeric matrix, especially if it is close to the glass transition temperature of the material. Increased molecular mobility would result in improved antimicrobial properties due to the enhanced release of the additive.

TABLE 5 Diffusion coefficient (D) and mass percentage of active compounds released at equilibrium with respect to the total mass in the film (M_{∞}/M_0) for several polymeric matrices with active compounds in contact with food simulants

Polymeric matrix	Active compound	Simulant A		Simulant B		Simulant D1		Simulant D2		Reference
		$D \times 10^{13}$ (m ² /s)	M_{∞}/M_0 (%)	$D \times 10^{13}$ (m ² /s)	M_{∞}/M_0 (%)	$D \times 10^{13}$ (m ² /s)	M_{∞}/M_0 (%)	$D \times 10^{13}$ (m ² /s)	M_{∞}/M_0 (%)	
PHBV	Carvacrol	3.2	22	2.8	23	7.2	96	0.15	65	Requena et al. (2017)
PHBV	Eugenol	0.5	47	0.5	52	5.5	92	0.023	71	Requena et al. (2017)
PLA-PHBV (blend)	Carvacrol	30	19	2	25	280	76	6	86	Requena et al. (2018)
PLA-PHBV/starch	Carvacrol	5	22	15	11	5	100	2	70	Requena et al. (2018)
PLA	Cinnamaldehyde	0.024	48	0.019	45	0.63	55	0.0031	5.5	Muller et al. (2017b)
PLA/starch	Cinnamaldehyde	0.53	35	0.15	29	13.8	27	0.018	8	Muller et al. (2017b)
Starch/PCL/starch	Carvacrol	3.9	75	5.3	57	46	100	100	96	Tampau et al. (2018)

Abbreviation: PCL, polycaprolactone; PLA, polylactic acid.

5.2 | Modeling release kinetics

For a given active compound, analyzing the release kinetics from a polymeric matrix into food simulants of varying polarities may help to predict the antimicrobial activity in a similarly polar food product. Several types of food simulants can be used. For example, 10% ethanol (Simulant A) and 3% acetic acid (Simulant B) aqueous solutions are used to simulate aqueous food matrices with pH values above and below 4.5, respectively. A 50% ethanol aqueous solution (Simulant D1) is used to simulate less polar matrices, such as oil–water emulsions or highly alcoholic products, and isooctane is used to simulate lipid matrices (Commission Regulation (EU) No 10/2011). Several authors (Muller et al., 2017b; Requena et al., 2017, 2018; Tampau et al., 2018) studied the release kinetics of EO compounds incorporated into biodegradable films using these four simulants. To this end, the amount of active compound released into the simulant as a function of contact time was modeled using a Fickian approach in terms of the mass of active compound released related to the total mass of the active compound in the film (M_t/M_0). Thus, the diffusion coefficient (D) and the mass of the active compound released at equilibrium (M_{∞}/M_0) were determined. Table 5 summarizes the obtained diffusion coefficient (D) and the released percentage at equilibrium of different active compounds incorporated into different polymeric matrices in contact with the abovementioned food simulants. Other mathematical models have been applied by different authors, such as first order kinetics (Tawakkal et al., 2016), Pep-

pas, and Weibull models (Bustos et al., 2016) or the Fick model (Tawakkal et al., 2016), to determine the release rate of active compounds and the maximum release at equilibrium. The models permit the concentration of the active substance reached in a food matrix with similar polarity at a given time to be estimated from a determined concentration of active substance incorporated into the packaging and a food/packaging mass ratio (Requena et al., 2017).

As can be observed in Table 5, both the release rate (diffusion coefficient, D) and release percentage of an active compound were greatly affected by both the polarity of the food simulant and the polymeric matrix. This is related to the different molecular interactions and chemical affinity between the active compound, the polymeric matrix, and the simulant. The diffusion coefficient of a determined compound from a polymer matrix was significantly affected by the polarity of the simulant as a consequence of the potential simulant migration into the film matrix and the resulting plasticization effect. Thus, the release of carvacrol and eugenol from the PHBV matrix was greatly promoted when the polarity of the simulant decreased (D1) due to both the higher degree of polymer relaxation in contact with the simulant and the greater affinity of active additives with the simulant, which contribute to a partition of the compounds that is more favorable to the simulant. In this sense, it is remarkable that there were differences between the release behavior of carvacrol and eugenol for the same polymer matrix and simulant; carvacrol was delivered faster but to a lower extent from PHBV than eugenol in every aqueous simulant, in line

with their different chemical affinity with polymer and simulants. In general, given the less polar nature of the active compounds, more compound is delivered when the simulant polarity decreases; however, considering the different polar and nonpolar phases present in the food systems, the release behavior can differ substantially in real foods, depending on the food structure. The film structure also has a great impact on the release kinetics and the concentrations at equilibrium. Therefore, particular molecular interactions inside the polymeric matrix and food system play an important role in the release kinetics of active compounds, and in complex systems, such as foods, it is difficult to easily predict the release behavior and antimicrobial effects. Therefore, specific release and antimicrobial studies are required to ensure the effectiveness of a determined potentially active material applied to a determined food system. These interactions become more complicated for multilayer films consisting of different polymeric layers, where the process is affected by the interactions and migration phenomena between interlayers and simulant/food. In fact, Requena et al. (2018) observed different carvacrol diffusion and equilibrium release in PHBV/PLA blend-starch bilayer films to that observed in PHBV monolayers (Table 5). Quiles-Carrillo et al. (2019) studied the release of gallic acid from electrospun fibers of PLA with and without a 10- μm PLA coating. The PLA coating acted as a barrier that affected the release kinetics; a sustained release was observed when the thin PLA barrier was used, whereas it was fast and abrupt otherwise. Similar results were reported by Neo et al. (2013) while electrospinning zein and gallic acid solutions, and the obtained fibers presented fast release with Fickian behavior.

6 | CONCLUSIONS

Biodegradable polymeric films coming from natural sources offer a promising alternative for the food packaging sector. Through the incorporation of different compounds into these matrices, active packaging materials can be obtained for specific applications, adding value to these materials with high production costs. In this sense, PAs represent an alternative to synthetic additives and EOs with a high sensory impact. Different polysaccharides and proteins have proven to have good properties as carriers of these active compounds, although their application is, in practice, limited by their highly hydrophilic nature. Studies into hydrophobic matrices, such as PLA, PHB, or PCL, with incorporated PAs are still scarce, but they point to the viability of these materials for application in high-water activity systems. Of the PAs, hydroxycinnamic acids exhibit antimicrobial activity regardless of the

substituents in the benzoic ring, while their antioxidant capacity is also enhanced when compared to their equivalent hydroxybenzoic acid. However, the specific molecular structure would also affect the release kinetics from the film into the food system due to the particular interactions between the active compound, the polymer matrix, and the food substrate. Therefore, although the prospects for future applications of PAs in active packaging seem promising, more research is required into the release kinetics and efficiency of different phenolic acid-polymer combinations when applied to specific real foods.

ACKNOWLEDGMENTS

The authors thank the Agencia Estatal de Investigación (Ministerio de Ciencia e Innovación, Spain) for the financial support through projects AGL2016-76699-R and PID2019-105207RB-I00. Author Ramón Ordoñez is grateful to the Honduras 2020 grant program for the support received.

AUTHOR CONTRIBUTIONS

Conceptualization, investigation, and writing—original draft: Ramón Ordoñez. Conceptualization, funding acquisition, project administration, supervision, writing—review and editing: Amparo Chiralt. Conceptualization, data curation, supervision, and writing—review and editing: Lorena Atarés.

CONFLICTS OF INTEREST

The authors declare no conflict of interest.

ORCID

Ramón Ordoñez,  <https://orcid.org/0000-0003-2672-5547>

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How to cite this article: Ordoñez, R., Atarés, L., & Chiralt, A. (2022). Biodegradable active materials containing phenolic acids for food packaging applications. *Comprehensive Reviews in Food Science and Food Safety*, 21, 3910–3930. <https://doi.org/10.1111/1541-4337.13011>