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Engineering Properties of Polymeric-Based Antimicrobial Films for Food Packaging

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Abstract The concept of antimicrobial packaging has received great attention because of its potential to enhance food safety. Several studies have explored its applications and effectiveness to suppress pathogenic microorganisms. However, few studies have analyzed the alterations caused in the engineering properties of food-packaging polymers after the incorporation of antimicrobials. Such information is very important to understand the feasibility of producing antimicrobial packaging films on the industrial scale. This review explores the work done so far to evaluate how the incorporation of antimicrobial substances affects the properties of food-packaging systems. This article also emphasizes diffusion studies on antimicrobial substances through packaging films and the analytical solutions used to characterize this diffusion mechanism. Our review found that although the properties of packaging materials are altered by the addition of antimicrobials such as organic acids, enzymes, and bacteriocins, every packaging material is unique, and these effects cannot be generalized.

Keywords Active packaging · Antimicrobial packaging · Gas barrier properties · Tensile strength · Thermal properties · Diffusion

Abbreviations

EVA	Ethylene-vinyl acetate
EVOH	Ethylene-vinyl alcohol
HDPE	High-density polyethylene
LDPE	Low-density polyethylene
PA	Polyamide (nylon)
PBAT	Poly(butylenes adipate-co-terephthalate)
PE	Polyethylene
PET	Polyethylene terephthalate
PLA	Poly(lactic acid)
PP	Polypropylene
PS	Polystyrene
PVC	Poly(vinyl chloride)
PVDC	Poly(vinylidene chloride)
PVOH	Poly(vinyl alcohol)
SEM	Scanning electron microscopy

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Introduction

Active packaging system involves interaction between the packaging material and the food to provide desirable effects and extend the shelf life of packaged foods. The food package interaction is achieved by the addition of certain additives into the packaging film to enhance the performance of the packaging system [31]. In recent years, great effort has been made to develop active packaging, of which the antimicrobial films have received great interest from the food industry to enhance the microbial safety of food. This interest in antimicrobial packaging is attributed to increasing consumer demand for minimally processed and additive-free foods [37].

Antimicrobial packaging refers to food-packaging systems that inhibit spoilage and reduce pathogenic microorganisms [9]. The packaging incorporated with antimicrobials helps extend the shelf life of foods by prolonging the lag period of microorganisms, thereby diminishing their growth and number. Antimicrobial packaging is intended to act against microorganisms and

enhance the functions of conventional food packaging, which are (1) shelf life extension, (2) maintenance of quality, and (3) safety assurance. For example, the contamination of refrigerated foods, which take place predominantly on the surface of the foods, can be prevented by the application of antimicrobial packaging materials [42].

Antimicrobial Technologies

A wide range of antimicrobial substances have been tested in laboratories for their potential applications in the antimicrobial food packaging. These substances include organic acids (benzoic acid, sorbates), enzymes (lysozyme, glucose oxidase), bacteriocins (nisin, pediocin), fungicides (benomyl, imazalil), polymers (predominantly chitosan), natural extracts, antibiotics, triclosan, and silver compounds. Each antimicrobial substance exhibits a unique mechanism of action that is specific to a particular range of foods and microorganisms. Some antimicrobials block or inhibit metabolic and reproductive processes of microorganisms, while others modify their cell wall conformation, leading to the loss of vital internal materials and adaptability in the medium. However, this can be a disadvantage for antimicrobial food-packaging systems, since an antimicrobial film may have limited applicability in certain food products. From a commercial standpoint, this may reduce marketing opportunities and potential applications [9, 10].

Commercially available antimicrobial materials contain mainly silver (Ag) and triclosan (2, 4, 4′-trichloro-2′-hydroxydiphenylether) as antimicrobial agents. In the first case, Ag cations bind with groups rich in electrons (containing sulfur, nitrogen, or oxygen), which can be found in DNA chains, for example. Such binding blocks vital biological processes for microbial survival and reproduction [42]. In the second case, triclosan may kill bacteria by altering the synthesis of lipids that form part of the cell wall [33]. Companies that currently offer antimicrobial materials containing Ag are DuPont (USA), Milliken Co. (USA), Surfacine Development Company (USA), and Ishizuka Glass Co. (Japan). Those that offer antimicrobial materials containing triclosan are Sanitized AG (Switzerland), Microban Products (UK), and Thomson Research Associates (Canada). However, the commercial application of these antimicrobial materials in the food-packaging industry is limited, mainly due to concerns about their applicability and safety [5, 42]. On the other hand, the medical sector and the textile industry have commercialized a number of different antimicrobial technologies, and thus this technology holds the potential for tremendous application in the food industry.

Antimicrobial Food-Packaging Films

Food-packaging films with antimicrobial activity can be divided into two groups: (1) films that allow the antimicrobial to migrate into the food (2) films that do not release antimicrobial substances and that inhibit microbial growth on the food surface [37]. In the first case, a preservative is found either within the matrix or on the surface of the food-packaging material. The corresponding substance can be released completely or in a specific amount on the food surface to perform its biocide action. Figure 1 shows a schematic representation for the first case in which (A) represents a packaging system that incorporates the antimicrobial agent in a single layer and releases it gradually into the food matrix, (B) represents the same concept but with an inner layer, which can be useful in controlling the release of the antimicrobial compound, and (C) consists of a layer of food-packaging material coated with a formulation containing an antimicrobial substance [9, 28]. In the second case, as it is shown in Fig. 1, the scheme (D) represents a packaging system in which antimicrobial activity occurs only when microorganisms get in contact with the surface of the packaging material [9, 28]. For both types of systems, direct contact with the food is necessary, making these technologies a suitable option for vacuum-packed foods such as cheese, meat, fish, or poultry [42]. The Microban™ System, created by Microban Products Co. (Huntersville, NC), is a commercially available antimicrobial plastic film using triclosan as the antibacterial additive. Microsphere® manufactured by Bernard Technologies, Inc. (Chicago, IL) is another example of a commercially available active film using chlorine dioxide as the antibacterial compound [42]. In Japan, films containing silver have been commercialized for food packaging [28]. Further research on developing new antimicrobial technology for the food-packaging industry is required to help increase the commercialization of antimicrobial food-packaging films.

Several studies have investigated the effectiveness of antimicrobial films against microbial growth. Nevertheless, some attempts to produce films with antimicrobial activity have failed, since many factors affect their ability to suppress microbial growth. The interaction of the antimicrobial agent with the corresponding packaging material may adversely affect the release of such an agent, or the film production procedure can diminish activity of the antimicrobial agent to levels that make it ineffective for its purpose. Processing operations used during the manufacture of packaging film, such as extrusion, printing, drying, or lamination, may significantly affect the activity of the antimicrobial compounds due to phenomena such as degradation and evaporation [37]. It is also important to consider the activity of the antimicrobial substance once it gets

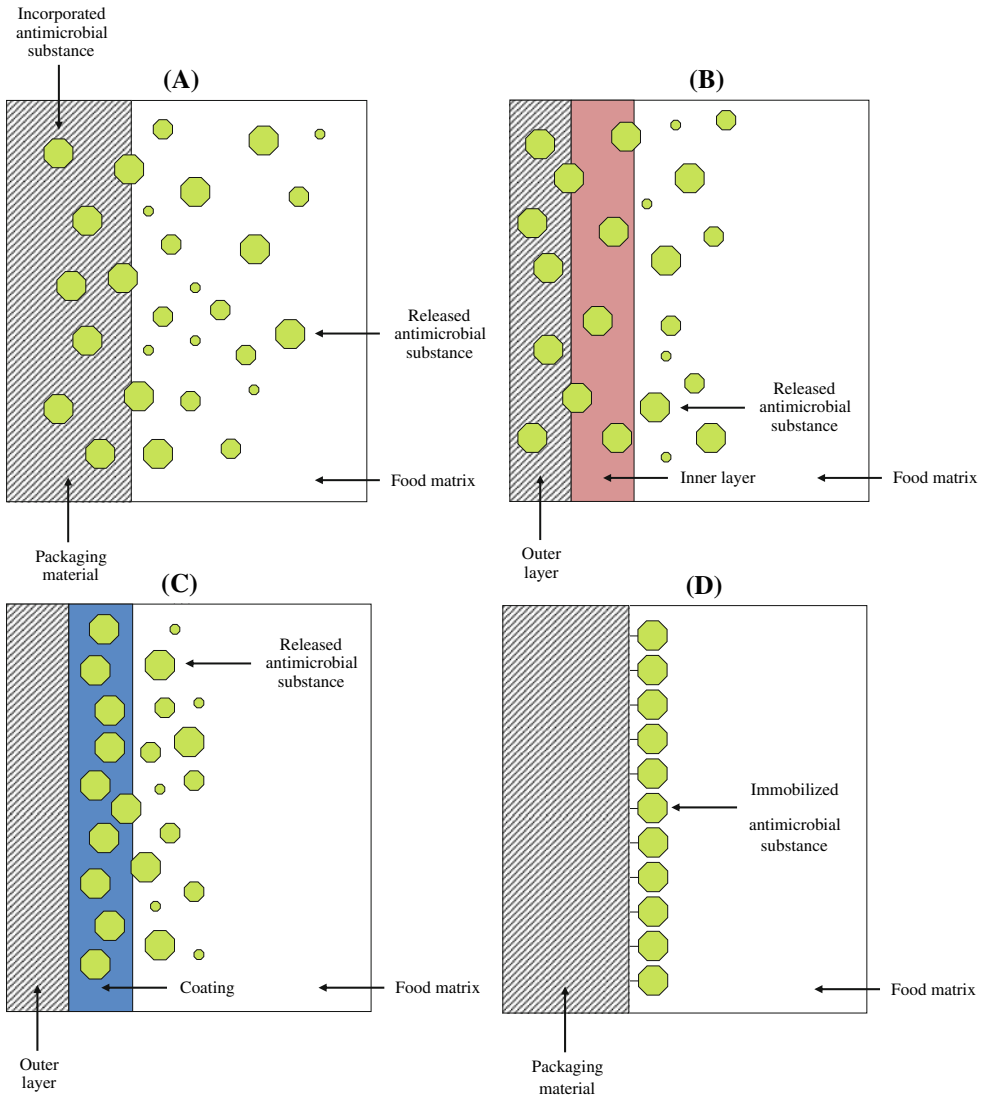

Fig. 1 Antimicrobial food-packaging systems (adapted from [9, 28]

in contact with the food matrix. The interaction between the antimicrobial substance and food components may be strong enough for the antimicrobial agent to become ineffective against the microorganisms it is intended to suppress. This may occur even when the effectiveness of the packaging material has been tested and confirmed in in vitro conditions [42].

Antimicrobial food-packaging films have been shown to influence the engineering properties of the film, such as the mass transfer properties of gases through the films, and the tensile, thermal, and morphological properties of these films. The level of influence depends on the type of film material, the film preparation procedure, and the antimicrobial agent used. These properties play an important role in determining the application of the film and the shelf life of the packaged food product. Modifications in the original properties of the film may be detrimental or even beneficial in the applicability of the packaging film, depending on the nature and extent of modification. However, to date, there has been no comparative analysis of the engineering properties of food-packaging films after the incorporation of antimicrobials. This review summarizes the importance of characterizing the diffusion of antimicrobials from packaging film to food, as well as the various models used to characterize the diffusion coefficient of antimicrobial food-packaging films.

Polymers Applied in Antimicrobial Food Packaging

Various polymers have been studied as potential candidates for incorporation of an antimicrobial substance in

Table 1 Density, melting point, and glass transition temperature of some common plastic films used in food packaging [3, 4, 18, 32]

Plastic	Density (g cm^{-3})	Melting temperature (°C)	Glass transition temperature (°C)
LDPE	0.915–0.935	120	-30 ± 15
HDPE	0.945–0.964	137	-30 ± 15
PP	0.90–0.91	168	-17 ± 5
PET	1.37	256–260	67–81
PS	1.04–1.12	250	80–100
PVOH	1.19–1.27	200–260	70–85
EVA	0.91–0.97		
PVC	1.39–1.43	180	80–100
PVDC	1.67–1.71	170–175	−17.5
PA	1.05–1.14	185–260	37–70

food-packaging applications. Synthetic polymers derived from petroleum have thus far dominated the applications in antimicrobial food-packaging films. Few biopolymers, which are produced by chemical synthesis from bioderived monomers, have been used in the production of antimicrobial films. A number of coatings and edible films derived from biopolymers have also been studied for antimicrobial applications. This article evaluates the properties of polymers derived from petroleum-based sources as well as those that are chemically synthesized, from bioderived polymers.

Synthetic polymers that have been used to develop antimicrobial food packaging films include PE, PP, PS, EVA, PVC, PA, and PBAT [14]. PLA is synthesized from bioderived monomers and can be applied as film for antimicrobial food packaging. The choice of antimicrobial polymeric film is based on the intended use of application, and hence depends on the properties of the polymeric films.

Packaging films derived from polymers exhibit a range of properties that makes them suitable for specific food applications. Table 1 presents the densities, melting temperatures (T_m), and glass transition temperatures (T_g) of several polymeric structures. The T_g, T_m, and crystallization temperature (T_c) are important thermal properties related to polymers used for food packaging, since they suggest the level of association between polymeric chains. These properties are also important for characterizing plastics for their use in food packaging and provide important information about some criteria that must be taken into account during processing [30]. Differential scanning calorimetry (DSC) is used to determine the thermal parameters of a polymer and characterize the crystallization mechanism of semicrystalline polymers. The degree of crystallinity (χ) is an important physical parameter that relates to the morphology and mechanical properties of the polymer [16].

Knowledge of the mechanical properties of polymeric structures is important for evaluating the quality of films intended for food packaging. The tensile properties generally evaluated are elastic modulus, tensile strength, and elongation at break. The elastic modulus is the force per unit area necessary to increase the length of a film sample to a specific extent. Tensile strength is the force per unit area applied when the film is broken, and the elongation at break is the percentage of change in the film length when the film is broken after a certain level of force is applied [32]. The measurement of the mechanical properties provides important information on the ability of packaging materials to sustain their integrity under the influence of various stresses that occur during the processing, handling, and storage of packaged foods [21]. To compare brittle and strong materials with those that are flexible or soft, method D882 from the American Society of Testing and Materials (ASTM) is used [30]. Table 2 shows the tensile properties of selected food-packaging materials at specific levels of relative humidity (RH) and temperature (T) [18, 32].

Another important parameter to consider when choosing polymeric films for food packaging is their permeability to oxygen and water vapor. These are important parameters to consider when deciding the type of packaging for a specific food product. All plastics are permeable to oxygen and water vapor to a certain degree [24]. Table 3 shows the water vapor and oxygen permeability for selected films used for food-packaging applications [22, 26].

Engineering Properties of Antimicrobial Food-Packaging Films

The properties of the food-packaging films are influenced after the incorporation of an antimicrobial substance. This section highlights changes in polymer film properties such

Table 2 Tensile properties of some common plastic films used in food packaging [18, 32]; Stenhouse et al. [36]

Plastic	Tensile strength			Elastic modulus			Elongation at break		
	Tensile strength (MPa)	T (°C)	RH (%)	Elastic modulus (GPa)	T (°C)	RH (%)	Elongation at break (%)	T (°C)	RH (%)
LDPE	7–25	20–25	65	0.15–0.34	20–25	65	300–900	20–25	65
HDPE	19–31	20–25	65	0.98	20–25	65	20–50	20–25	65
PP	27–98	20–25	65	1.18	20–25	65	200–1000	20–25	65
PET	157–177			3.5			70	20–25	65
PS	31–49	20–25	65	2.7–3.4	20–25	65	2–3	20–25	65
PVOH	39–118			2.9	20–25	65	225	20–25	65
EVA	6–19	20–25	65				230–560	20–25	65
PVC	42–55	20–25	65	2.8	20–25	65	20–180	20–25	65
PVDC	49–98	20–25	65	0.2–0.6	20–25	65	10–40	20–25	65
PA	49–69	20–25	65	0.7–0.98	20–25	65	200–300	20–25	65
EVOH	55–65			2.0–2.3			100–225		

Table 3 Oxygen and water vapor permeability of some common plastic films used in packaging [17, 22, 26]

Plastic	Oxygen permeability (OP)			Water vapor permeability (WVP)		
	OP × 10^7 (mL m m^{-2} day^{-1} Pa^{-1})	T (°C)	RH (%)	WVP × 10^{14} (g m m^{-2} s^{-1} Pa^{-1})	T (°C)	RH (%)
LDPE	44.756	25		6.673–8.704	38	100
HDPE	7.127	25		1.741–3.482	38	90
PP	4.936–9.869	23	50	2.321–4.642	23	85
PET	0.098–0.494	23	50	5.803–22.921	23	85
PS	9.869–14.805	23	50	11.315–45.552	23	85
PVOH	0.003	23	0	342.652	23	85
EVA	21.220	23		6.673–17.118		
PVC	0.198–0.790	23	50	18.279	38	90
PVDC	0.001–0.030	23	50	1.161	23	65
PA	0.010–0.098	30	60	5.803–114.314	23	65

as mechanical, gas barrier, thermal, and morphological alterations.

Mechanical Properties

A significant change can be obtained in the tensile properties of polymeric films after the incorporation of antimicrobials. Table 4 exhibits some studies in which the tensile properties were evaluated in polymeric films after incorporating antimicrobials. Significant changes in the characteristics of the films can be expected, since the incorporation of antimicrobial agents in a food also leads to changes in some important properties [9].

According to Han and Floros [11], a significant effect in the tensile properties is not expected when the molecular weight of the antimicrobial molecule is smaller than that of the polymeric material. In such a case, the incorporation of the antimicrobial should not alter the conformation of the packaging material's polymer structure, thereby not influencing its tensile properties. However, even small quantities of the corresponding antimicrobials can change the tensile properties (Table 4), if they interact with the packaging material's matrix [20, 25, 41]. A decrease in film strength and resistance was observed with increase in concentration of the antimicrobial incorporated in the polymer [20, 27]. On the other hand, improvement in tensile properties was observed in PVOH films

Table 4 Tensile properties of polymeric films incorporated with antimicrobials

Film	Antimicrobial	Antimicrobial incorporation method	Tensile properties without the antimicrobial substance			Tensile properties with the antimicrobial substance			Source
			Elastic modulus (KPa)	Tensile strength (KPa)	Elongation at break (%)	Elastic modulus (KPa)	Tensile strength (KPa)	Elongation at break (%)	
PE/PA/PE	Nisin	Solution coating with HPMC (hydroxypropyl methylcellulose)	110*		271*	420*		130*	Guiga et al. [8]
Multilayer polyethylene film	Silver nanoparticles (0.6% w)	Lamination and extrusion	27,000		460	24,000		445	Sánchez-Valdez et al. [34]
Multilayer polyethylene film	Silver nanoparticles (0.6% w)	Blending through sonication and solution-casting method	27,000		460	25,500		495	Sánchez-Valdez et al. [34]
Multilayer polyethylene film	Silver nanoparticles (0.6% w/w)	Spraying	27,000		460	26,000		480	Sánchez-Valdez et al. [34]
Cellulose derivative polymer	Natamycin formulation (8% w/w)	Blending and solution-casting method		0.09*	4.54*		0.0573*	1.69*	Pires et al. [25]
Cellulose derivative polymer	Nisin formulation (50% w/w)	Blending and solution-casting method		0.09*	4.54*		0.0260*	1.03*	Pires et al. [25]
Cellulose derivative polymer	Natamycin and Nisin formulation (8% and 50% w/w, respectively)	Blending and solution-casting method		0.09*	4.54*		0.0113*	0.72*	Pires et al. [25]
Vinylidene chloride copolymer	Sorbic acid (1.5% w/v)	Blending and solution-casting method		34,032.52*	11.9		20,753.22*	16.2	Limjaroen et al. [20]
Vinylidene chloride copolymer	Sorbic acid (2% w/v)	Blending and solution-casting method		34,032.52*	11.9		20,580.85*	15.4	Limjaroen et al. [20]
Vinylidene chloride copolymer	Sorbic acid (3% w/v)	Blending and solution-casting method		34,032.5*	11.9		19,594.90*	16.7	Limjaroen et al. [20]
Vinylidene chloride copolymer	Potassium sorbate (2% w/v)	Blending and solution-casting method		34,032.5*	11.9		13,251.72*	12.7	Limjaroen et al. [20]
Vinylidene chloride copolymer	Potassium sorbate (3% w/v)	Blending and solution-casting method		34,032.5*	11.9		8,673.60*	13.9	Limjaroen et al. [20]
Vinylidene chloride copolymer	Nisin (1% w/v)	Blending and solution casting		34,032.5*	11.9		7 191.23*	11.1	Limjaroen et al. [20]
Vinylidene chloride copolymer	Nisin (2% w/v)	Blending and solution casting		34,032.5*	11.9		6,563.81*	10	Limjaroen et al. [20]
Vinylidene chloride copolymer	Nisin (2.5% w/v)	Blending and solution casting		3,4032.5*	11.9		5,488.23	11	Limjaroen et al. [20]

Table 4 continued

Film	Antimicrobial	Antimicrobial incorporation method	Tensile properties without the antimicrobial substance			Tensile properties with the antimicrobial substance			Source
			Elastic modulus (KPa)	Tensile strength (KPa)	Elongation at break (%)	Elastic modulus (KPa)	Tensile strength (KPa)	Elongation at break (%)	
Methyl cellulose	Natamycin (2 mg/10 g of film-forming solution)	Blending and solution casting	313,230	36,630	73.98	380,730	37,170	60.45	Türe et al. [41]
Methyl cellulose	Natamycin (20 mg/10 g of film-forming solution)	Blending and solution casting	313,230*	36,630*	73.98	299,900*	22,590*	56.76	Türe et al. [41]
PBAT	Nisin (1,000 IU cm^{-2})	Blending and solution casting	47,700*	18,700*	513	29,000*	13,200*	512	Bastarrachea et al. [1]
PBAT	Nisin (3,000 IU cm^{-2})	Blending and solution casting	47,700*	18,700*	513	24,900*	11,800*	458	Bastarrachea et al. [1]
PBAT	Nisin (5,000 IU cm^{-2})	Blending and solution casting	47,700*	18,700*	513	22,900*	11,100*	448	Bastarrachea et al. [1]
Pectin/PLA (75%/25%)	Nisin (1% w/v of film-forming solution)	Coating	2.5×10^6	53,400	3	2.6×10^6	40,200	1.98	Jin et al. [13]
EVA/LDPE	Thymol (4% w/v)	Solution coating		10,300*	1,018.86		8,250*	964.64	Tippayatum et al. [40]
EVA/LDPE	Eugenol (4% w/v)	Solution coating		10,300*	1,018.86		8,550*	938.20	Tippayatum et al. [40]
EVA/LDPE	Thymol + Eugenol (4% w/v)	Solution coating		10,300	1,018.86*		9,440	914.04*	Tippayatum et al. [40]

IU international units

* Significant difference ($P < 0.05$) in the corresponding property between the films with and without antimicrobial

incorporated with enterocin, and this increase could be attributed to the fact that the antimicrobial enterocin acts like a plasticizer for the PVOH films, thereby increasing the flexibility of the films [21].

Gas Barrier Properties

Changes in gas barrier properties of polymeric films containing antimicrobials have not been extensively evaluated. A possible reason for a lack of such studies could be that during development of antimicrobial films, the effectiveness of antimicrobials against pathogenic microorganisms is determined and optimized before other properties of the films are evaluated. Tables 5 and 6 show the gas barrier properties of films incorporated with antimicrobials obtained in previous works. It is evident that the incorporation of antimicrobials can generate a significant effect, although this is not always a negative effect. For example, Table 5 shows that the incorporation of antimicrobials may actually improve gas barrier properties. Suppakul et al. [38] suggest that this may be caused by an increase in hydrophobicity of the system, leading to a lower permeability to water vapor. Table 6 highlights the changes in the water vapor barrier properties of films after the incorporation of active components. According to Robertson [30], the transmission of gases through a packaging material can take place through two mechanisms: pore effect and solubility-diffusion effect. In the first case, the gases cross the material by passing through small pinholes or ruptures in the structure. In the second case, the concentration difference between the two sides of the packaging material and the solubility of gases in the corresponding material determines the level of transmission. It appears that antimicrobials affect the structure of food-packaging films, thereby affecting the permeability of gases by changing their solubility or due to the creation of pinholes in the packaging structure. However, the final effect depends on the type of antimicrobial agent incorporated and polymeric structure, and generalizations cannot be made.

Thermal Properties

Table 7 highlights how incorporating antimicrobials affects the thermal properties of food-packaging films. Limited studies have evaluated the thermal properties of antimicrobial food-packaging films, and no significant changes in the T_g and T_m have been observed after the incorporation of antimicrobials [1, 40]. However, the overall crystallinity of PBAT films has been shown to decrease significantly with an increase in nisin concentration to 5,000 IU/cm^2. This change in crystallinity has been used to describe the variations in the tensile properties of antimicrobial films [1]. Thus, there is a definite need for further research to measure the thermal properties of food-packaging films containing antimicrobials. This would help elucidate the interaction of polymers with antimicrobials and also help researchers set processing parameters for fabrication of active films.

Morphological Properties

Surface morphology of antimicrobial films has been studied using the scanning electron microscopy (SEM) technique. Micrographs of film surfaces help explain structural modifications induced by the incorporation of antimicrobials in the polymer matrix. In some cases, the addition of antimicrobials could lead to the formation of pores in the polymer matrix, thereby influencing the tensile and gas barrier properties of the film. Figure 2 shows environmental scanning electron microscopy (ESEM) images of PBAT films with and without the addition of nisin as the antimicrobial agent. The authors noticed the formation of small holes and pores in PBAT films incorporated with nisin as the interaction between the antimicrobial agent and the polymer interrupted bond formation in the PBAT molecule [1]. Figure 3 shows SEM images of three polymeric films before and after the addition of the antimicrobial agent. The interaction of the antimicrobial with the polymer leads to the formation of cavities in the PVOH films, whereas void spaces develop from the interaction of enterocin with alginate films [21]. Hence, microscopy images help us understand the differences in the film morphology due to the addition of the antimicrobial component. These morphological changes could cause significant changes in other engineering properties of the film, but the level of changes is difficult to generalize and depends on the particular polymer–antimicrobial interaction.

Diffusion of Antimicrobials Through Food-Packaging Polymers

During the evaluation and characterization of antimicrobial food-packaging films, it is important to investigate the diffusion of antimicrobial substances through packaging films. This information helps us determine how likely a packaging film can hold antimicrobial substances and release them when they come in contact with food [23]. According to Han [10], studying the release of antimicrobial components from packaging materials is fundamental, since this determines how well microorganisms are eliminated. The release should not be slower than the microbial growth.

An important factor to consider is the solubility of the antimicrobial substance in selected foods. If the solubility is very high, the release may take place rapidly, quickly

Table 5 Oxygen permeability (OP) and oxygen transmission rate (OTR) of polymeric films incorporated with antimicrobials

Film	Antimicrobial	Antimicrobial incorporation method	OP $\times 10^7$ before the incorporation of the antimicrobial (mL m m^{-2} day^{-1} Pa^{-1})	OP $\times 10^7$ after the incorporation of the antimicrobial (mL m m^{-2} day^{-1} Pa^{-1})	OTR $\times 10^3$ before the incorporation of the antimicrobial (mL m^{-2} day^{-1})	OTR $\times 10^3$ after the incorporation of the antimicrobial (mL m^{-2} day^{-1})	T (°C)	RH (%)	Source
Vinylidene chloride copolymer	Sorbic acid (1.5% w/v)	Blending and solution-casting method	5,260.3	3,306.2			23	0	Limjaroen et al. [20]
Vinylidene chloride copolymer	Sorbic acid (2% w/v)	Blending and solution-casting method	5,260.3	5,664.9			23	0	Limjaroen et al. [20]
Vinylidene chloride copolymer	Sorbic acid (3% w/v)	Blending and solution-casting method	5,260.3	8,507.3			23	0	Limjaroen et al. [20]
Vinylidene chloride copolymer	Potassium sorbate (2% w/v)	Blending and solution-casting method	5,260.3*	444.1*			23	0	Limjaroen et al. [20]
Vinylidene chloride copolymer	Potassium sorbate (3% w/v)	Blending and solution-casting method	5,260.3*	>453,984*			23	0	Limjaroen et al. [20]
LDPE	Linaool (1% w/w)	Extrusion			9.2*	6.1*	23	0	Suppakul et al. [38]
LDPE	Methylchavicol (1% w/w)	Extrusion			9.2*	4.7*	23	0	Suppakul et al. [38]
PBAT	Nisin (1,000 IU cm^{-2})	Blending and solution casting	4.80	10.7			23	0	Bastarrachea et al. [1]
PBAT	Nisin (3,000 IU cm^{-2})	Blending and solution casting	4.80	7.54			23	0	Bastarrachea et al. [1]
PBAT	Nisin (5,000 IU cm^{-2})	Blending and solution casting	4.80	11.3			23	0	Bastarrachea et al. [1]

IU international units

* Significant difference ($P < 0.05$) in the corresponding property between the films with and without antimicrobial

Table 6 Water vapor permeability (WVP) and water vapor transmission rate (WVTR) of polymeric films incorporated with antimicrobials

Film	Antimicrobial	Antimicrobial incorporation method	WVP $\times 10^{14}$ before the incorporation of the antimicrobial (mL m m^{-2} s^{-1} Pa^{-1})	WVP $\times 10^{14}$ after the incorporation of the antimicrobial (mL m m^{-2} s^{-1} Pa^{-1})	WVTR before the incorporation of antimicrobial (g m^{-2} day^{-1})	WVTR after the incorporation of antimicrobial (g m^{-2} day^{-1})	T (°C)	RH (%)	Source
Vinylidene chloride copolymer	Sorbic acid (1.5% w/v)	Blending and solution-casting method	110.3*	308.7*			37.8	90	Limjaroen et al. [20]
Vinylidene chloride copolymer	Sorbic acid (2% w/v)	Blending and solution-casting method	110.3*	330.8*			37.8	90	Limjaroen et al. [20]
Vinylidene chloride copolymer	Sorbic acid (3% w/v)	Blending and solution-casting method	110.3*	441.0*			37.8	90	Limjaroen et al. [20]
Vinylidene chloride copolymer	Potassium sorbate (2% w/v)	Blending and solution-casting method	110.3*	815.9*			37.8	90	Limjaroen et al. [20]
Vinylidene chloride copolymer	Potassium sorbate (3% w/v)	Blending and solution-casting method	110.3*	837.9*			37.8	90	Limjaroen et al. [20]
LDPE	Linaool (1% w/w)	Extrusion			13.7*	10.5*	38	90	Suppakul et al. [38]
LDPE	Methylchavicol (1% w/w)	Extrusion			13.7*	5.2*	38	90	Suppakul et al. [38]
PBAT	Nisin (1,000 IU cm^{-2})	Blending and solution casting	3.04	3.49			25		Bastarrachea et al. [1]
PBAT	Nisin (3,000 IU cm^{-2})	Blending and solution casting	3.04	3.40			25		Bastarrachea et al. [1]
PBAT	Nisin (5,000 IU cm^{-2})	Blending and solution casting	3.04	3.61			25		Bastarrachea et al. [1]

IU international units

* Significant difference ($P < 0.05$) in the corresponding property between the films with and without antimicrobial

Table 7 Thermal properties of polymeric films incorporated with antimicrobials

Film	Antimicrobial	Antimicrobial incorporation method	Thermal properties without the antimicrobial substance				Thermal properties without the antimicrobial substance				Source
			T_c (°C)	T_g (°C)	T_m (°C)	χ (%)	T_c (°C)	T_g (°C)	T_m (°C)	χ (%)	
PBAT	Nisin (1,000 IU cm^{-2})	Blending and solution casting	59.2*	−36.3	122	10	69.8*	−36.5	123	10.6	Bastarrachea et al. [1]
PBAT	Nisin (3,000 IU cm^{-2})	Blending and solution casting	59.2*	−36.3	122	10*	69.1*	−36.3	124	7.38*	Bastarrachea et al. [1]
PBAT	Nisin (5,000 IU cm^{-2})	Blending and solution casting	59.2*	−36.3	122	10*	70.7*	−36.6	124	5.28*	Bastarrachea et al. [1]
EVA/ LDPE	Thymol (4% w/v)	Solution coating		−28.8	61.3	1.9		−25.2	58.8	2.1	Tippayatum et al. [40]
EVA/ LDPE	Eugenol (4% w/v)	Solution coating		−28.8	61.3	1.9		−30.2	63.6	2.8	Tippayatum et al. [40]
EVA/ LDPE	Thymol + Eugenol (4% w/v)	Solution coating		−28.8	61.3	1.9		−31.0	64.0	2.4	Tippayatum et al. [40]

IU international units

* Significant difference ($P < 0.05$) in the corresponding property between the films with and without antimicrobial

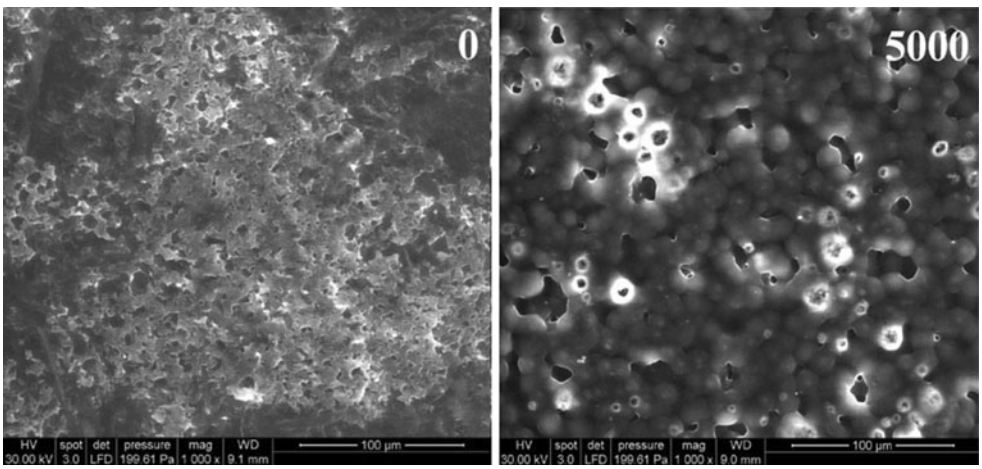

Fig. 2 Electron microscopy images of PBAT with the nisin concentration in IU/cm^2. The holes and pores can be observed as dark spots (reproduced with permission from [1]. Copyright 2010 IFT Publisher)

decreasing the antimicrobial concentration on the food's surface. On the other hand, if the solubility is low, the antimicrobial may accumulate on the food's surface and migrate slowly through the food matrix. Both scenarios relate to the diffusion coefficient (D) of the antimicrobial through the food. Both scenarios also depend on the value of D held by the corresponding antimicrobial in the packaging material. The diffusion characteristics of antimicrobials can be used to determine the amount necessary to maintain concentration levels above the minimum inhibitory concentration [10].

Chemical and physical factors are related to the diffusion of antimicrobial substances through packaging materials. This diffusion may be influenced by hydrogen bonds, ionic bonds, ionic osmosis, hydrophobic interactions, electrostatic interactions, and so on. The configuration of the films' matrix and its implications, like the presence of a tortuous and porous medium, can also influence the diffusion phenomenon [23].

Several studies have evaluated the diffusion of antimicrobial substances in food-packaging films [2, 6, 12, 15, 29, 39, 43]. Fick's second law models release behavior, and depending on testing conditions, different analytical solutions can be applied to calculate the value of D. Table 8 exhibits the analytical solutions for Fick's second law utilized in previous works to calculate the value of D at a specific temperature (T). These studies were performed at different temperatures to characterize the behavior of D as

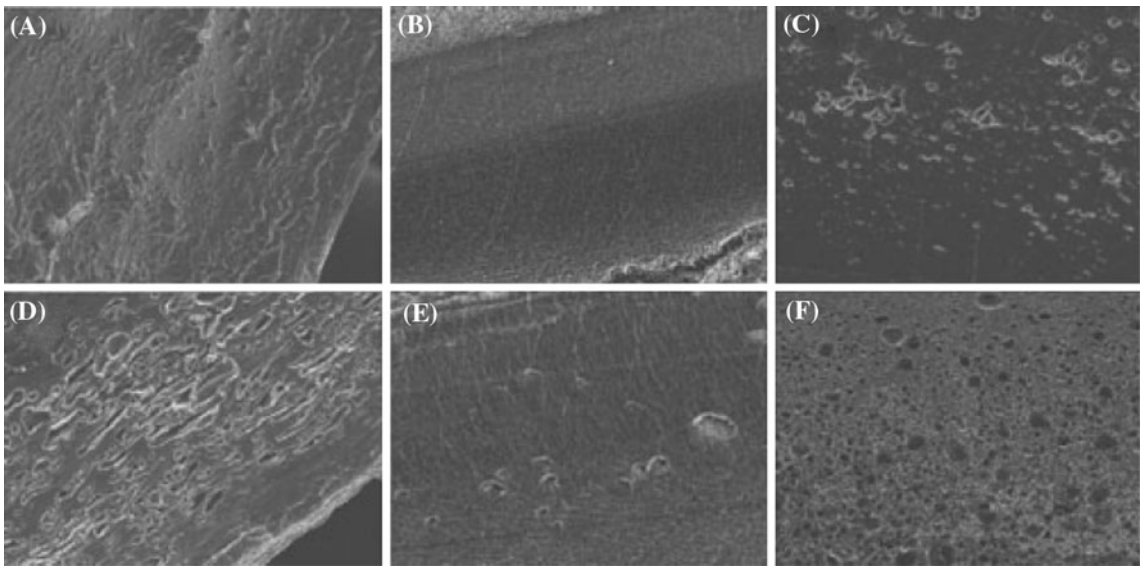

Fig. 3 Scanning electron microscopy (*SEM*) micrographs of cross-sections of biodegradable films obtained at different magnifications: control alginate (**a**), polyvinyl alcohol (PVOH) (**b**), and zein (**c**) films; enterocin containing alginate (**d**), PVOH (**e**), and zein (**f**) films. Magnifications of × 700 (**a**), × 450 (**b**), × 1,100 (**c**), × 1,500 (**d**), × 600 (**e**), and × 250 (**f**) (reproduced with permission from [21]. Copyright 2010 IFT Publisher)

a function of that parameter. Generally, the value of *D* increases with temperature, thereby raising the release of the antimicrobial. This can be advantageous since the proliferation of microorganisms' increases as temperature rises as well, which can be controlled if the release of the antimicrobial substance also increases. The study of the release kinetics of antimicrobials and the application of mathematical models to fit the data obtained can be a useful tool for making predictions in food-packaging systems with antimicrobial activity [23].

Commonly, the *D* of antimicrobials through the film matrix is lower than in foods. This may lead to a shelf life prolongation since small amounts of the antimicrobial would be transferred to the food, diminishing the number of microorganisms. This could also imply the utilization of smaller quantities of antimicrobials and a consequent reduction in the production costs, as well as an increase in profits due to extended shelf life [23].

Han and Floros [12] studied the migration of potassium sorbate through LDPE, PET, PP, and HDPE (Table 8). In that study, the films were placed in the middle of a cell divided into two chambers. One of the chambers contained a solution with a known concentration of potassium sorbate. The diffusion of potassium sorbate was studied by analyzing its concentration from the other chamber. In several studies involving commonly used synthetic films, the method of incorporation of the antimicrobial substance has been by coating the film with a solution containing the antimicrobial [7, 19], while in others it has been possible to incorporate directly the substance in the film matrix [1, 2, 35]. This suggests that it is not always possible to incorporate the studied antimicrobial directly in the films' matrix. If this is the case, it would be necessary to take into account the coating layer rather than the plastic material to determine diffusion.

Final Remarks

The increasing consumer demand for minimally processed and additive-free food has led to a great interest in the development of antimicrobial-based active food-packaging films. Antimicrobial food packaging has been shown to be effective for inhibiting pathogenic microorganisms and thereby improving food safety. However, antimicrobial substances can affect the engineering characteristics of packaging films, which may affect their applicability.

This review highlighted the changes in film properties after the incorporation of antimicrobials in the polymer matrix. Many studies have shown that significant changes occur in mechanical, thermal, and gas barrier properties as well as surface morphology when these antimicrobials are incorporated. It is important to study the interaction of the antimicrobial components with polymeric chains, since the level of interaction varies from case to case. Limited studies measure the change in overall crystallinity in terms of thermal parameters. This review stresses the need to measure these parameters in order to understand the processability of active packaging films.

Table 8 Values of D obtained in previous studies using different analytical solutions of Fick's second law

Film	Antimicrobial substance	Fick's second law analytical solution utilized	$D \times 10^{12}$ ($cm^2\ s^{-1}$)	T (°C)	Reference
LDPE	Potassium sorbate	$\frac{C(x,t)}{C_1} = \left(1 - \frac{x}{l}\right) + \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{C_1}{n}\sin\left(\frac{n\pi x}{l}\right)e^{\left(-\frac{Dn^2\pi^2 t}{l^2}\right)}$	18,300	25	Han and Floros [12]
PET (biaxially oriented)	Potassium sorbate		0.543	25	Han and Floros [12]
PP	Potassium sorbate	$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty}\frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2}e^{\left(-\frac{Dq_n^2 t}{l^2}\right)}$	0.465	25	Han and Floros [12]
HDPE	Potassium sorbate		0.426	25	Han and Floros [12]
Cellulose acetate	Lysozyme		150–2,330	4	Gemili et al. [6]
Sodium alginate	Potassium sorbate		232,000–318,000	25	Zactini and Kieckbusch [43]
Wheat gluten	Sorbic acid		31,000	4	Redl et al. [29]
Wheat gluten with beeswax	Sorbic acid		41,000	10	Redl et al. [29]
Wheat gluten with distilled acetylated monoglycerides	Sorbic acid		75,000	20	Redl et al. [29]
Wheat gluten	Sorbic acid	$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty}\frac{8}{(2n+1)^2\pi^2}e^{\left(-\frac{D(2n+1)^2\pi^2 t}{l^2}\right)}$	22,000	4	Redl et al. [29]
Wheat gluten with beeswax	Sorbic acid		30,000	10	Redl et al. [29]
Wheat gluten with distilled acetylated monoglycerides	Sorbic acid		56,000	20	Redl et al. [29]
Wheat gluten	Sorbic acid		16,000	4	Redl et al. [29]
Wheat gluten with beeswax	Sorbic acid		22,000	10	Redl et al. [29]
Wheat gluten with distilled acetylated monoglycerides	Sorbic acid		32,000	20	Redl et al. [29]
Cast corn zein	Nisin	$\frac{M_t}{M_0} = 1 - 4\left(\frac{Dt}{h^2}\right)^{\frac{1}{2}}\left\{\pi^{-\frac{1}{2}} + 2\sum_{n=1}^{\infty}(-1)^n ierfc\frac{nh}{\sqrt{Dt}}\right\}$	7	5	Teerakarn et al. [39]
Cast corn zein	Nisin		77	25	Teerakarn et al. [39]
Cast corn zein	Nisin		310	35	Teerakarn et al. [39]
Cast corn zein	Nisin		640	45	Teerakarn et al. [39]
Wheat gluten	Sorbic acid		31,000	4	Redl et al. [29]
Wheat gluten with beeswax	Sorbic acid		41,000	10	Redl et al. [29]
Wheat gluten with distilled acetylated monoglycerides	Sorbic acid		75,000	20	Redl et al. [29]
Wheat gluten	Sorbic acid	$\frac{M_t}{M_\infty} = 4\left(\frac{Dt}{h^2}\right)^{\frac{1}{2}}\left\{\pi^{\frac{1}{2}} + 2\sum_{n=1}^{\infty}(-1)^n ierfc\frac{nh}{\sqrt{Dt}}\right\}$	22,000	4	Redl et al. [29]
Wheat gluten with beeswax	Sorbic acid		30,000	10	Redl et al. [29]
Wheat gluten with distilled acetylated monoglycerides	Sorbic acid	$\frac{M_t}{M_\infty} = 4\left(\frac{Dt}{\pi h^2}\right)^{\frac{1}{2}}$	56,000	20	Redl et al. [29]
Wheat gluten	Sorbic acid		16,000	4	Redl et al. [29]
Wheat gluten with beeswax	Sorbic acid		22,000	10	Redl et al. [29]
Wheat gluten with distilled acetylated monoglycerides	Sorbic acid		32,000	20	Redl et al. [29]
Acrylic polymer	Nisin	$\frac{M_t}{M_\infty} = \frac{2}{h}\left(\frac{Dt}{\pi^2}\right)^{\frac{1}{2}}$	4	10	Kim et al. [15]
Vinyl acetate ethylene copolymer	Nisin		9	10	Kim et al. [15]
PBAT	Nisin	$\frac{M_{St}}{M_{F,0}} = \frac{\alpha}{1-\alpha} - \sum_{n=1}^{\infty}\frac{2\alpha}{1+\alpha+\alpha^2 q_n^2}e^{\left[-\frac{Dq_n^2 t}{l^2}\right]}$	0.93	5.6	Bastarrachea et al. [2]
PBAT	Nisin		2.29	22	Bastarrachea et al. [2]
PBAT	Nisin		5.78	40	Bastarrachea et al. [2]

C, concentration of the antimicrobial substance at time t and position x through the film; C_1, initial concentration of the antimicrobial substance in the film; M_t, released amount of the antimicrobial substance at time t; M_∞, released amount of the antimicrobial substance at equilibrium; l, film's thickness; α, ratio between the volumes of the solution and the film; q_n, positive root of $\tan q_n = -\alpha q_n$; M_0, initial amount of antimicrobial in the film; M_t, released amount of the antimicrobial substance at time t; M_∞, released amount of the antimicrobial substance at equilibrium; h, film's thickness; *ierfc*, associated function of the mathematical error function (*erfc*); $M_{S,t}$, amount of antimicrobial in the solution at time t; $M_{F,0}$, amount of antimicrobial in the film at $t = 0$; α, ratio between the volumes of the solution and the film; q_n, positive root of $\tan q_n = -\alpha q_n$; l, half of the film's thickness

Studies on the release of antimicrobial substances will help researchers understand the mechanisms of liberation of active components from packaging films. More research is necessary to take advantage of the breakthroughs made thus far in this area. Improving the properties of antimicrobial packaging systems and determining in which foods they work best with will maximize their usefulness, cost-effectiveness, and safety.

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