Sorption, diffusivity, permeability and mechanical properties of chitosan, potassium sorbate, or nisin incorporated active polymer films

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Abstract The active multilayer packaging films were formed from low-density polyethylene (LDPE) and polyamide containing a 2% antimicrobial agent in one of the LDPE sides of the film (LDPE/polyamide/LDPE-2% antimicrobial agent). The antimicrobial agents used were potassium sorbate (PS-film), nisin (N-film), or chitosan (CTS-film). The effects of antimicrobial incorporation on water vapor permeability (P), diffusivity (D_{eff}), and solubility (S_o and S_H) of the active and control films (LDPE/polyamide/LDPE) were investigated. A dynamic vapor sorption analyzer (DVS) was used to estimate the sorption isotherms of the films at 25 °C. Peleg was found to be the best equation to describe sorption behaviors. The addition of PS and nisin into the film matrix resulted in a lower P than that of the control film. The D_{eff} values of the active films were lower than those of control films, except for the CTS-film. The high water-holding capacity of PS and nisin might limit the D_{eff} of the respective films. It was found that Henry's law was applicable to relate P , D_{eff} , and S_o and S_H values of the multilayer film [correlation coefficient (r) = 0.909–0.971]. The mechanical and thermal properties of the active films were not significantly affected by the incorporation of PS and nisin ($p > 0.05$). However, the impact of stress and elongation (transverse direction) on the CTS-film was lower than on other films, which

indicated that chitosan improved the mechanical properties of the film.

Keywords Antimicrobial active film · Sorption · Diffusion · Permeability · Mechanical and thermal properties

Introduction

Food packaging can take an active role in food safety during the storage of a product since antimicrobial agents can be incorporated into polymer packaging films to enhance food safety in terms of human health (Barzegar et al. 2014). This relatively new packaging technology has been called “antimicrobial active packaging system.” The types of polymers and the additives that are used are important for characterizing the structural and barrier properties of packaging materials (Bastarrachea et al. 2011).

The incorporation of antimicrobials into film materials can affect the physical and barrier properties, can change the hydrophilicity/hydrophobicity of the film matrix related with the characteristics of the ingredients (Bastarrachea et al. 2011). Some studies have been conducted to observe these properties of multilayer or multi-blended films (Smith et al. 2006; Mittal 2013; Chytiri et al. 2006; Garofalo et al. 2018). Smith et al. (Smith et al. 2006) produced polyethylene oxide (PEO)/poly-acrylic acid (PAA) films as poly-layered (90 layer-by-layer), and they suggested that behavior of both inorganic and organic thin films and coatings can be affected by remaining moisture after drying and curing process or gained moisture the environment in which the product is stored or in use. Mittal (2013) produced nanocomposite films with PE or

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polypropylene and examined their properties, and they reported that structure of the matrix must be examined in details to predict the barrier properties. Garofalo et al. (2018) published an article characterizing a nanocomposite multilayer packaging film that was formed with PE and nano-clay incorporated polyamide. They found that the presence of nano-clays in the polyamide layer ensured a significant improvement in the oxygen barrier and the mechanical properties of multilayer films. Rhim et al. (2013) had reported that silver incorporation caused a significant decrease in the P of agar nanocomposite films by increasing the surface's hydrophobicity. Accordingly, it was found by Barzegar et al. (2014) that the addition of PS had increased the P of starch-clay composite films, due to increasing polar hydrophilic groups in the film. Despite, it was reported that nisin concentration did not affect the P of active LDPE films coated with hydroxypropyl methylcellulose containing nisin. In terms of mechanical properties, Remedio et al. (2019) had claimed that chitosan films were modified with the addition of antimicrobial agents such as PS or nisin.

Water sorption and diffusion in polymers are complex phenomena that need to be investigated in order to estimate the practical application of food packaging materials for different food systems and their different storage conditions since if films have raised hydrophobicity, they would have lower permeability to water vapor (Suppakul et al. 2013). Briefly, a few works of literature had reported diffusion kinetics of water vapor in single-layer polymer films (Barzegar et al. 2014; Rhim et al. 2013; Remedio et al. 2019; Fukuda 1996; Metayer et al. 1999), some composite films (Liu et al. 2018; Reddy et al. 2018) and bilayer films from LDPE and polyamide (Garofalo et al. 2018). The effects of the diffusion of water vapor through films have also been reported in some studies (Sarkar et al. 2018), but the authors are unaware of the presence of data examining water vapor diffusivity and MSI of multilayer active films.

This study aimed to investigate the effects of PS, N, or CTS incorporation on WVTR, P , D_{eff} , and solubility properties of LDPE-polyamide multilayer films in the form of LDPE-polyamide-LDPE having antimicrobial agents on one side of LDPE. Oxygen barriers and thermal and mechanical properties of the multilayer active polymer packaging films were also analyzed to characterize the films.

Materials and methods

Materials

Nisin and chitosan were obtained from Handary SA, and PS was obtained from Aldrich Chemical Company, Inc.,

USA. All other reagents were analytical grade and obtained from Merck (Darmstadt, Germany).

Methods

Film production

For the production of multilayer active films, primarily antimicrobial additives were mixed with PE pellets, and these masterbatches were to form the active side of the films (Soysal et al. 2015). The active LDPE layer was formed by mixing 2% antimicrobial agents (chitosan, nisin, or PS) with polyethylene pellets (94%), 2% orevac as a tie layer, and 2% ethylene–vinyl acetate copolymer (EVA), using a twin-screw extruder. The active-multilayer (LDPE-polyamide-active LDPE) and control (LDPE-polyamide-LDPE) films of the same thicknesses (70 μm) were produced using a blown film extrusion process. The optimization of processing conditions and of the concentration of antimicrobials was part of a project (project number: 3110257) supported by TUBITAK Industrial. We couldn't give some details about the extrusion systems due to this limitation.

DVS measurement

The MSI of the polymer films was measured using Dynamic Vapor Sorption (DVS) Intrinsic (Surface Management Systems, London, UK). The samples were dried entirely in DVS to reach 0% RH, and then they were exposed to a stepwise increase in RH from 0 to 90% in 10% increments and back down to 0% RH to observe the moisture adsorption and desorption characteristics of films at 25 °C. The weight of the samples was ~ 15 –20 mg, and equilibrium was considered to be reached when d_m/d_t (changes in mass with time) was 0.001%/min. The Guggenheim–Andersen–de Boer (GAB), Peleg, Oswin, and Halsey models were applied to determine the best fit for adsorption and desorption isotherms of films. Detailed calculations and equations to define MSI properties of films were given as:

$$\text{GAB} : m = \left(\frac{m_0 C k a_w}{(1 - k a_w)(1 - k a_w + k C a_w)} \right)$$

$$\text{Oswin} : m = a \left(\frac{a_w}{(1 - a_w)} \right)^b$$

$$\text{Halsey} : m = \left(\frac{a}{(\ln(a_w))} \right)^{1/r}$$

$$\text{Peleg} : m = k_1 (a_w^{n_1}) + k_2 (a_w^{n_2})$$

where m = equilibrium moisture content; m_o = monolayer moisture content; C = Guggenheim constant; k = factor

correcting properties of multilayer molecules corresponding bulk liquid; a , b , r , k_1 , k_2 , n_1 , and $n_2 = \text{constant}$.

Measurement and calculation of water diffusivity coefficient

The diffusivity constant (D_{eff}) of water vapor through films was evaluated from DVS data obtained after drying samples completely at 0% RH and exposing samples directly to 90% RH at 25 °C. The initial slopes of sorption isotherms were used to determine the effective diffusion constant (D_{eff}) for each film type. The diffusivity of water vapor was evaluated using an equation based on Fick's second law because the layer obtained in the study was assumed to be a thin, one-directional layer (Eq. 1) (Chen et al. 2019; Redl et al. 1996).

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp\left[-(2m+1)^2 \pi^2 T\right] \quad (1)$$

where M_t and M_∞ are amounts of water vapor absorbed at time t and at infinite time, respectively; they were calculated using data from the DVS apparatus from 0 to 90% RH. M_∞ was defined when the mass of samples change versus time was < 0.002 mg/min (“ m ” is a mathematical/trigonometric variable).

The equation valid for early stages ($M_t/M_\infty < 2/3$) of diffusion was used to calculate the diffusivity constant (Eqs. 2 and 3):

$$\frac{M_t}{M_\infty} = 4 \times \left(\frac{D \times t}{\pi l^2}\right)^{0.5} \quad (2)$$

$$D_{\text{eff}} = \left(\frac{kl}{4}\right)^2 \pi \quad (3)$$

where l is film thickness, and k is the slope of linear regression of (M_t/M_∞) against $t^{1/2}$.

The power-law model was applied to investigate the mechanism involved in the diffusion process for a planar system by fitting an early portion of release curve:

$$\frac{M_t}{M_\infty} = kt^n \quad (4)$$

where M_t is amount of water at time t at M_∞ is equilibrium at infinite time, k is a constant that characterizes macromolecular network system, and n is a diffusional exponent feature of diffusion mechanism. For $n \leq 0.5$, the diffusion mechanism follows Fick's law (Rubilar et al. 2017). This type of diffusion is called Case I or Fickian diffusion, and its release rate depends on $t^{0.5}$.

Measurement of water vapor transmission rate

ASTM F1249-13 method was performed to determine WVTR using Permetran Model C 4/41 (Mocon, Inc., Minneapolis, Minn., USA). Three specimens for each film (size 10×10 cm, thickness 70 μm) were measured, and the mean was reported. The detection limit of the device was 0.05 g/m²day. The test conditions of WVTR were 0–90% RH at 25 °C.

P was calculated using the following equation (Eq. 5) in terms of g cm/cm²s cmHg of films:

$$P = \frac{\Delta m}{(\Delta t)(\Delta p)(A)} \times l \quad (5)$$

where l is the thickness of films (cm), A is the film area (m²), Δp is the difference in the partial pressure of water vapor between the two sides of the film (kPa), and Δm represents film weight differences at a specific time interval (Δt).

Solubility calculations

According to Henry's law of solubility, there is a linear relationship between external vapor pressure and corresponding concentration within the surface of plastic film (Miller and Krochta 1997). The relationship between permeability and solubility has been commonly extrapolated from a linear sorption isotherm. If one assumes the diffusion coefficient to be constant under studied RH conditions, then the relationships among coefficients, diffusivity, permeability, and solubility can be defined by the equation below (Eq. 6).

The solubility coefficient (cm³/cm³cmHg), S_o , was calculated using following (Eq. 6) (Lin and Freeman 2004):

$$P = D \times S_o \quad (6)$$

where D (cm²/s) refers to the diffusion coefficient of water vapor from 0 to 90% RH, which was calculated according to the theoretical aspects presented in Section “DVS measurement”.

Assuming that Henry's law was obeyed for the solubility (S_H) of water vapor in films, then an adsorption isotherm can be used to calculate S_H from the slopes of isotherms, as suggested by Van Krevelen, Te Nijenhuis (Van Krevelen and Te Nijenhuis 2009) and (Eq. 7):

$$S_H = \frac{22400 \times \rho(\text{polymer})}{M(\text{water})} \times \frac{1}{p(\text{vapor})} \times b_m \quad (7)$$

where p is partial pressure of water vapor (cm Hg), 22,400 cm³/mole is molar volume of water vapor at STP, M is molecular weight of water, ρ is the density of the polymer (g/cm³), and b_m (mg H₂O/mg film, per unit relative pressure) is the slope of the MSI model that best fits

the experimental points (Van Krevelen and Te Nijenhuis 2009).

The true densities of our films (ρ), which were needed for Eq. 7, were measured by a hydrostatic weighing method using an Ohaus balance that was equipped with a density kit (NJ, USA), according Lin and Freeman (2004):

$$\rho = \frac{M_A}{M_A - M_L} \times \rho_o \quad (8)$$

where M_A and M_L represent the film's weight in the air and the film's weight in liquid, respectively (Lin and Freeman 2004).

The TPV values were calculated from the true density and bulk density of films using the following equation (Eq. 8) (Otoni et al. 2016):

$$TPV = \frac{\rho_t - \rho_b}{\rho_t \times \rho_b} \quad (9)$$

where: ρ_t = true density; ρ_b = bulk density.

Characterization of physicochemical properties of films

The thermal behavior of films was measured using a Hitachi DSC 7000× (Tokyo, Japan) differential scanning calorimeter (DSC). Indium was used to calibrate the instrument. A 7 mg sample was accurately weighed and sealed in an aluminum pan. Samples were heated up to 600 °C at 20 °C/min, using N₂ as a purge gas.

Thermal measurements (thermogravimetric analysis-TGA) were also performed using a Hitachi TGA system (Tokyo, Japan) at a heating rate of 20 °C/min under nitrogen atmosphere, starting at 20 °C, up to 600 °C. The differential thermogravimetric (DTG) curve that is the first derivative of TGA curve was obtained from the TGA instrument software directly.

Tensile properties were determined using the ASTM method (ASTM D882-91 test method) using an Instron Testing Machine Model 441 (Norwood, Massachusetts, USA). Five samples of each film were analyzed regarding tensile stress, elongation, and modulus of elasticity.

Scanning electron microscopy (SEM) visualization

Films were analyzed using an FEI, Quanta 650 Field Emission SEM microscope, equipped with a high-resolution field emission gun. Film samples were cut into 10 mm × 10 mm pieces, which were fixed on top of the spice holder by using double-sided adhesive tape and then coated with gold. The samples were examined at 20 kV and a magnification of 500 ×.

Statistical analysis

The slopes of the adsorption isotherms, linear and nonlinear regression analyses were evaluated using Sigma Plot for Windows 12.3 (2011 Systat Software, Inc.). All experiments were performed in triplicate, and mean values were represented. The statistical differences among the means were determined by Tukey's multiple range tests at a significance level of 5%, using SPSS 19.0 (SPSS Inc., Chicago, IL) statistical program.

Results and discussion

Moisture sorption isotherm

Adsorption isotherms of the active and control films are illustrated in Fig. 1. Raj et al. (2002) showed that the LDPE film did not exhibit any moisture sorption, and Broudin et al. (2015) showed that the MSI of polyamide displayed an upward curvature, which became more and more pronounced at a higher RH, with no initial curvature at low RH values. Hence, the reason for increasing the moisture adsorption of control films with increasing RH might be related to the presence of polyamide in its inherent hydrophilic structure: The C=O structure in the polyamide backbone might promote an affinity of the films to water (Garofalo et al. 2018).

It was found that the equilibrium moisture content of PS-films stored at all a_w ranges studied was higher than that of control or active films. The addition of PS might cause additional hydrophilicity compared to the control film; hence, moisture could be bound by the film without any visually detected physical change in the structure. This result had also been observed by Chowdhury and Das (2010) and reported as PS blending into starch-based film

Fig. 1 Moisture adsorption isotherms of control and active films

and causing a slight increase in equilibrium moisture content.

All film types had hysteresis; hysteresis of PS-film was higher than control and/or active films, especially at 60%, 70%, and 80% RH values. Higher hysteresis values might indicate more water molecules were retained in the film matrix during desorption (Otoni et al. 2016) due to possible changes in the capillary structure of film by addition of PS. The incorporation of nisin and chitosan into film matrix did not cause any significant change when compared to the control film in terms of hysteresis ($p > 0.05$).

When Fig. 1 was examined, it could be seen that the sorption behaviors of all studied films were BET type II. Type II isotherm is sigmoidal sorption in which curves are concave; it usually indicates the existence of multilayers at internal surface of a material (Andrade et al. 2011; Peleg 2019), and in practice, it can be representative of sorption of water in hydrophilic polymers. Results of nonlinear regression analysis for data from GAB, Oswin, Halsey, and Peleg equations were shown in Table 1. The GAB and Peleg models gave the best R^2 and RMSE values for describing relationship between moisture content and a_w of films.

The GAB model presented some critical parameters, such as monolayer moisture content (m_0), which has been the most frequently applied model for MSI description (Suppakul et al. 2013; Peleg 2019). The m_0 of control films, showing to be strongly bound water, was 0.780% on a dry basis. The presence of polyamide in the LDPE layers resulted in a higher hydrophilic character than plain LDPE film due to its amide functional group; it led to a possible change in m_0 (Broudin et al. 2015). Broudin et al. (2015) reported m_0 value for polyamide as 0.05%, which was also lower than our result. LDPE is a strong water-vapor barrier; however, it still allows some water vapor molecules to pass through it. If water vapor passed through both sides of LDPE and were adsorbed by polyamide (which could be described as enveloping polyamide with LDPE), more water was bound by the polyamide than expected.

It was observed that the value of m_0 increased with the addition of the PS into the film, confirming that the addition of PS led to increasing hydrophilicity of the film. Unexpectedly, the m_0 values of CTS-film and N-film were lower than those of the control film since chitosan and nisin have a high moisture-adsorption capacity. However, there was no significant difference between the m_0 values of the films studied.

Table 1 Estimated parameters and criteria for comparing sorption equations of control and active films

Equation	Constants and criteria	Film types							
		Control film		PS- film		N- film		CTS- film	
		Adsorption ^{a*}	Desorption ^a	Adsorption ^a	Desorption ^b	Adsorption ^a	Desorption ^b	Adsorption ^a	Desorption ^b
GAB	m_0	0.780	0.766	0.811	2.035	0.586	0.779	0.692	0.736
	C	3.346	2.481	2.041	1.526	3.810	5.522	2.733	5.428
	K	0.760	0.741	0.833	0.592	0.849	0.765	0.764	0.720
	R^2	0.9986	0.9983	0.9928	0.9937	0.9993	0.9983	0.9986	0.9995
	RMSE	0.024	0.018	0.071	0.068	0.048	0.054	0.078	0.027
Oswin	m	0.830	0.994	0.838	1.101	0.751	0.956	2.106	2.003
	b	0.458	0.374	0.561	0.450	0.521	0.419	0.771	0.566
	R^2	0.9843	0.9883	0.9828	0.9655	0.9937	0.9869	0.9835	0.9842
	RMSE	0.081	0.064	0.110	0.160	0.109	0.106	0.266	0.166
Halsey	a	− 0.470	− 0.635	− 0.515	− 0.778	− 0.420	− 0.595	− 0.351	− 0.450
	r	1.784	2.153	1.481	1.820	1.584	1.937	1.710	2.049
	R^2	0.9572	0.9663	0.9677	0.9378	0.9787	0.9656	0.9618	0.9583
	RMSE	0.127	0.112	0.150	0.214	0.299	0.236	0.350	0.292
Peleg	k_1	0.954	1.239	0.839	0.353	1.102	1.084	0.794	1.197
	n_1	0.623	0.531	0.577	0.102	0.766	0.539	0.652	0.668
	k_2	1.750	1.391	2.979	2.966	2.067	1.768	1.603	1.113
	n_2	3.123	3.290	3.819	1.946	40,673	3.102	3.197	3.458
	R^2	0.9999	0.9991	0.9969	0.9972	0.9998	0.9999	0.9999	0.9999
	RMSE	0.008	0.003	0.047	0.045	0.014	0.011	0.016	0.013

*superscripts a and b: with different letters indicate a significant difference between adsorption and desorption data (Tukey test, $p < 0.05$)

The Peleg model is a mathematical model used to describe isotherms, and it does not offer to describe physicochemical parameters, like the GAB model does (Suppakul et al. 2013). However, due to the presence of a large number of variables in the model, it was found to be the best fit since it could be used to predict the sorption behavior of films considering the R^2 and RMSE values. Oswin's and Halsey's models did not give a fit as good as the other models, although they were advised to define type II and type III isotherms (Andrade et al. 2011).

Water vapor transmission, permeability, and solubility of films

The WVTR of the control film was 10.1 g/m² per day (Table 2). The literature reported the WVTR values of plain LDPE and polyamide as 15–23 g/m² per day (50–75 µm) and 194 g/m² per day (50–75 µm), respectively (Cao et al. 2020; Battisti et al. 2017). Garofalo et al. (2018) postulated that the WVTRs of bilayer polyamide/PE film with different tie agents was between 2.5–3.0 g/m² per day, with thicknesses of 60–80 µm at 85% RH. The differences between our reported results could arise from the differences in the composition and structure of the films that were formed, as well as the measurement conditions. Chytiri et al. (Chytiri et al. 2006) observed that the WVTR of bilayer LDPE-recycled LDPE films, with a thickness of 80 µm, was in the range of 1.0–1.5 g/m² days.

The addition of antimicrobials (Table 2) into the film structure significantly decreased the WVTR of the films, except for the CTS-film ($p < 0.05$). Barzegar et al. (2014) also observed a similar improvement in the behavior of PS and nisin in starch-clay nano-composite films. In another study, blending of nisin into sodium caseinate films resulted in better water vapor barrier properties (Kristo et al. 2008).

There were significant differences between the P values of the films (Table 2, $p < 0.05$). The presence of PS decreased the P to almost 18% of the value of the control film, as a result of possible binding of water vapor with PS in the film structure, as seen in the sorption isotherms. A similar tendency was also observed for the P of N-film, which was 21% lower than the control film. Having lower P values of PS and N-films might have resulted in greater water-holding capacity of PS and nisin; however, that of the CTS-films was similar to the control films.

Chitosan has a polysaccharide origin, and it was expected that chitosan-containing films would have higher P ; however, the P of CTS film could occur in an unforeseen way. It was reported that water clusters were not observed in the chitosan structure: All the water was adsorbed by the hydrophilic sides of chitosan, with no further water retention (Chalykh et al. 2014). According to these reports, it might be possible to state that P could be limited by increasing the water-retaining ability of the film. Chitosan can act as filler in the film structure. A filler can be placed into gaps to improve the P of films, which was also reported by Mittal (2013).

The permeation of polymer by small molecules depends on both molecular diffusion and molecule solubility (S), and knowing the solubility value of a polymer can help to control the permeability of water vapor. Solubility can be described by the distribution of a permeate molecule between the surface of a polymer and the surrounding headspace, and it can offer crucial information about the amount of substance (gas) per unit volume of solvent (polymer) in equilibrium with a unit partial pressure (Smith et al. 2006; Miller and Krochta 1997). Since the solubility of water vapor in a film structure is a function of temperature (S_o) and vapor pressure (S_H) (Miller and Krochta 1997), a current study has tried to calculate the solubility values S_o and S_H of films using two equations (Eqs. 6, 7) from various data such as D , P , and sorption slopes, which

Table 2 Water vapor transmission rate (WVTR), water vapor permeability (P), diffusivity (D), solubility (S), true density (ρ_t), total pore volume (TPV) and thermal stability of control and active films*

Film type**	WVTR	OTR***	D	S_o	S_H	P	ρ_t	TPV	TGA results (°C)			DSC results (°C)			$\Delta H(\text{kJ/kg})$
									$T_{25\%}$ *	$T_{50\%}$ *	T_e *	T_g	T_o	T_m	
Control Film	10.1 ^a	20.9 ^a	1.61 ^a	2.4 ^a	12.08 ^b	3.89 ^a	0.9812 ^b	0.150 ^b	440.8	461.4	490.4	53.4	78.0	111.9	50.9 ^a
PS- Film	8.15 ^b	3.00 ^c	1.37 ^b	2.3 ^a	12.66 ^a	3.14 ^c	0.9854 ^b	0.155 ^b	443.0	468.0	498.6	53.9	81.0	110.4	47.2 ^a
N-Film	7.95 ^b	7.5 ^b	1.18 ^c	2.6 ^a	12.97 ^a	3.07 ^c	0.9829 ^b	0.153 ^b	443.3	463.7	497.7	53.3	85.8	114.5	45.3 ^a
CTS- Film	9.55 ^a	9.3 ^b	1.68 ^a	2.0 ^b	11.55 ^b	3.38 ^b	0.9951 ^a	0.164 ^a	441.6	463.4	500.0	54.4	85.8	144.4	43.8 ^b

*WVTR: g/m² day; OTR: cc/m² day; D : 10⁻¹⁰ cm²/s; S : cm³/cm³cmHg; P : 10⁻¹⁰ g cm/cm²cmHg s; ρ_t : g/cm³

**a and b values: with different letters within lines indicate significant difference between values (Tukey test, $p < 0.05$)

***From Soysal et al. (2015)

were obtained by executing different methods. S_o and S_H are listed in Table 2.

There was a strong relationship between these two S values ($r = 0.8526$). Hence, they could each refer to predict the solubility feature of a film according to the studied variables; both calculated coefficients, that was, S_H and S_o , were interpretable. As seen in Table 2, control films had higher S_o and S_H than N-films, as was expected from their P values. Considering this, it could be said that with increasing P values, S values decreased, and water vapor was distributed through the film structure. S of CTS-film was not different from that of control film, which could indicate water clustering or spreading might not occur in control and CTS-films. Chalykh et al. (2014) indicated that all water molecules were absorbed onto active centers of polysaccharides, which resulted in no water clustering in such systems.

The barrier properties of a film mainly depend on the chemical and three-dimensional morphological structures of films (Fukuda 1996). During film production, morphological structure can change by forming some voids and pores that may allow the mass transfer of gas. In literature, some studies reported that the addition of small molecules in blends could lead to the filling of a small void in a polymer matrix and/or obstructs movement of gas or vapor molecules (Otoni et al. 2016). Total pore volume (TPV) represents the porosity of the film using a relationship between its bulk and true densities (Otoni et al. 2016).

Because our multilayer film was composed mainly of LDPE (contain 2.9% polyamide), the ρ_b of our films was assumed to be the same value for densities of the amorphous phase of polyethylene equal to 0.855 g/cm^3 (Flaconneche et al. 2001) to calculate TPV using Eq. 9. The ρ_t values of films were measured using the method mentioned before (Section “Solubility calculations”), and the calculated results can be found in Table 2.

Since there was no significant difference between TPV values of active films and control film (except CTS-film), it might be interpreted that the morphological structure did not affect the barrier properties of films. Thus, the better barrier features of the active film could be explained by the molecules’ permeating through the polymer matrix itself due to the chemical structure features of films rather than the micro-pathway model, which was based on a morphological structure (Otoni et al. 2016). Also, gas molecules can diffuse easier from stiffer molecules than more elastic ones with a similar morphological structure (Mittal 2013).

Diffusion of water vapor

The apparent diffusivity (D_{eff}) of the multilayer films studied was calculated using Fick’s second law equation;

Fick’s second law was applicable for gaseous diffusion in a planar and thin sheet and in one direction (Eq. 1) (Redl et al. 1996). In our study, it was assumed that Fick’s law was also applicable to calculate the D_{eff} values of the films since the n values were less than 0.5. At the same time, when different transport mechanisms occur, it becomes difficult to separate individual mechanisms, as the rate of moisture movement can be described by an apparent diffusivity (D_{eff}). D_{eff} , without considering to which mechanism it corresponds, represents net moisture movement. D_{eff} of water vapor through films was calculated from the DVS data obtained at RH conditions from 0 to 90% at 25 °C, and diffusion kinetics of water vapor through films were evaluated using techniques given by Enrione et al. (2007), and Messin et al. (2019).

D_{eff} values of active and control films were listed in Table 2. D_{eff} of the control film was $1.61 \times 10^{-10} \text{ cm}^2/\text{s}$ while the D value of LDPE film was reported as $7.42 \times 10^{-8} \text{ cm}^2/\text{s}$ at 25 °C (Metayer et al. 1999) while water diffusivity of polyamide (PA6.6) varied between 1 and $14 \times 10^{-10} \text{ cm}^2/\text{s}$ (Broudin et al. 2015). Differences in D values might be due to the presence of both LDPE and polyamide in the film matrix. Similarly, it was reported that while D of PE and polyamide were $1.6 \times 10^{-7} \text{ cm}^2/\text{s}$ and $1.97 \times 10^{-9} \text{ cm}^2/\text{s}$, respectively, polyamide/PE film was $1.51 \times 10^{-6} \text{ cm}^2/\text{s}$ (Mittal 2013).

The incorporation of PS and nisin has led to the improvement of water vapor barrier properties since the D_{eff} values of the PS-film and N-film were 15% and 27% lower than that of control films, respectively. The presence of PS in films might cause the binding of water molecules. Hence, water vapor transmission and diffusion might be limited. If the polymer contains a hydrogen-bonding side such as PS-films, diffusivity can be decelerated since PS-adsorbed water could become more immobile because of partial dissolution (Van Krevelen and Te Nijenhuis 2009; Enrione et al. 2007). Moreover, the D_{eff} value of the N-film was lower than that of the control film. Nisin has an amphiphilic cationic (having hydrophilic and hydrophobic sides) nature. Therefore, the diffusion of water vapor first occurred in the form of water molecule penetration into the film matrix. Later, water molecules could be bound by nisin and remain in the film. On the other hand, the D_{eff} values of control and chitosan were not very different.

It was found that there was a particular relationship between the D_{eff} and WVTR values ($r = 0.909$). The strongest correlation was found between WVTR and S_H ($r = 0.971$), followed by similar correlations of WVTR and P ($r = 0.928$). These findings clearly showed that the water vapor transmission depended on the P , D_{eff} and S values of the film. Also, it could be said that examining the solubility behavior of a film would help predict the water vapor barrier properties of a film since there is a strong

Fig. 2 DSC (a), TGA/DTG (b) curves of control and active films

correlation between these two values ($r = 0.971$). There were different conclusions related to the effect of RH on water vapor diffusion throughout the film: For instance, Metayer et al. (1999) suggested that D coefficients did not depend on permeate concentration, and this behavior of molecular diffusion in a polymer was indicated as Fickian behavior. Besides, Basiak et al. (2017) showed that there was a specific interaction between water (permeate) and hydrophilic film. These differences might arise from the

full diversity of film bases such as petroleum or/and biodegradable-based films.

Thermal and mechanical properties

In the DSC thermograms were given in Fig. 2, the first peak showed glass transition temperature (T_g), and the second was the melting peak. Glass transition temperature (T_g), melting onset (T_o), melting (T_m), and the final melting temperature (T_f) of films were tabulated in Table 2. There

were no significant differences between control and active films in DSC thermograms.

T_m of control and active films were slightly lower than LDPE itself, which was between 115 °C and 241 °C. This could vary based on the cross-linkages of the polyethylene bonds in the structure (Van Krevelen and Te Nijenhuis 2009; Flaconneche et al. 2001). On the other hand, similarly to our result, it was reported that multilayered LDPE/LDPE films had T_m values that were approximately 110 °C (Chytiri et al. 2006). The T_m value depended on intermolecular forces within the blend, and if the bonds are broken easily, the film will have a low T_m . Van Krevelen and Te Nijenhuis (2009) suggested that when the T_g/T_m ratio is lower than 0.5, polymers are highly symmetrical and have small repeating units that consist of one or two central chain atoms, which indicates excellent polymer properties. The T_g/T_m ratios of all films were lower than 0.5; hence, it may be said that the addition of antimicrobial agents and multilayer films did not have any adverse effects on structural properties.

The ΔH values of the active films (except the N-film) were not statistically different from those of control films ($p > 0.05$). This indicates that the addition of antimicrobial agents into film matrixes did not lead to any change in the thermal stability of the films. However, the ΔH of the N-film was significantly different from other films ($p < 0.05$).

The thermal stability of films was also evaluated using TGA (Fig. 2). The temperature at 25% weight loss ($T_{25\%}$), the temperature at 50% weight loss ($T_{50\%}$), and the temperature end of degradation (T_e) were tabulated in Table 2. The thermal degradation of films started at 480 °C, and this was not affected by the incorporation of antimicrobials in LDPE. It is also worth noting that thermal decomposition temperatures of LDPE and polyamide polymer films were near 380 °C (Van Krevelen and Te Nijenhuis 2009). Considering the result, it might be said that the thermal stability of films was improved with the production of multilayer polymer films containing LDPE and polyamide.

The thermal stability of a film is affected by intramolecular forces; if the atom–atom bonds within the molecule broke easily, thermal stability would be lower. It was found that the mass loss of active films was not different from that of control films, which was similar to the DSC results. Another graph obtained from TGA thermograms was the DTG curve, which was used to estimate material loss versus temperature (Fig. 2). There were not many differences among films, but the DTG curve of the PS-film had a shoulder that might be related to the degradation of PS.

The mechanical properties of active and control films were tabulated in Table 3. There was no significant difference between the mechanical properties of films except for the CTS-film. It was accepted that the mechanical properties of an active packaging film depended on the addition of quantity and kind of antimicrobials, the molecular weight of antimicrobial agents, and the interaction between polymer and antimicrobials, as well as the solubility of antimicrobials into a blend (Bastarrachea et al. 2011). Furthermore, if the molecular weight of an antimicrobial molecule is smaller than the used polymer matrix (Bastarrachea et al. 2011), no change in tensile properties is expected, as in the case of our study (Table 3). However, chitosan incorporation caused improvement in some mechanical properties of the film. This could be explained by the incorporation of an antimicrobial agent with a film matrix. Under this condition, it could be expected that tensile strength and elongation at the break would be unchanged or changed positively, similar to the results for the CTS-film (Table 3): The impact stress of CTS-film was significantly higher than that of other films due to the excellent film-forming ability of chitosan. This result might have arisen from the capability of chitosan to act as a filler in the matrix (Garofalo et al. 2018). In parallel with our results, Chytiri et al. (2006) also found TS of multilayer films (LDPE/LDPE) to be from 16.5 to 21.4 MPa. Moreover, the elongation of multilayer films comprises polyamide/PE that was measured as 51–60% (Garofalo et al. 2018).

Table 3 Mechanical properties of control and active film

Film type*	Ultimate stress (N/m ²)		Elongation (%)		Modulus (N/m ²)		Tensile stress (N)		Impact Stress (N)
	MD**	TD**	MD	TD	MD	TD	MD	TD	
Control Film	63.8	67.9	125.8	88.1 ^b	757.3	713.6	16.9	16.8	144.9 ^b
PS- Film	69.9	67.9	126.9	85.9 ^b	753.0	768.9	16.8	16.8	150.9 ^b
CTS- Film	72.9	67.0	137.5	121.3 ^a	733.9	721.6	16.9	16.9	213.7 ^a
N-Film	68.1	75.5	124.7	97.9 ^b	787.3	716.0	17.1	16.9	140.4 ^b

*MD machine direction of film, TD transverse direction of the film

**a and b values: with different letters within lines indicate a significant difference between values (Tukey test, $p < 0.05$)

Fig. 3 SEM micrographs of multilayer films at $500\times$ $\oplus$ outer layer; $\equiv$ central layer; $\odot$ inner-active layer

SEM Imaging of Surfaces and the Cross-Sections of Films

A SEM analysis of the active and control films was performed to confirm the dispersion and presence of antimicrobials, and the images confirmed the presence of antimicrobials in the films. SEM micrographs of the sample are shown in Fig. 3. PS was uniformly dispersed within the active side of the multilayer film and the sizes of the PS molecules ranged between 2.5 and 3.4 μm , indicating an excellent distribution. As seen in Fig. 3, chitosan and nisin had larger molecule sizes than PS; nevertheless, an excellent distribution of these agents in LDPE was also observed. It could be concluded that all of the antimicrobial agents that were analyzed in this study were appropriate additives for producing an active film that is formed with LDPE. The multilayer structures of the films can be seen in the cross-section images in Fig. 3.

Conclusion

The Peleg and GAB equations were found to be good models for describing the MSI behaviors of films. The addition of PS and nisin into the film matrix resulted in lower WVTRs than those of the control film, resulting in improved film barrier properties. The strong correlation between the two S values (S_o and S_H) was examined in the current study. Both S values of the N-films were found to be higher than those of the control. The D_{eff} values of PS and N-films were 15% and 27% lower than those of control multilayer films. A comparison of correlation coefficients revealed that Fick's second law and Henry's law may be applied to evaluate P , D , and S for multilayer active films and to estimate interactions. The impact of stress and elongation (TD) on CTS-film was higher than on other films, indicating the chitosan-improved mechanical properties of the film. It might be stated that all active film types studied can be used as a food packaging material for food products stored in all ranges of RH, as the incorporation of agents did not reveal any barrier or structural problems.

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