

Preparation and characterization of LDPE/PVA blend films filled with glycerin-plasticized polyvinyl alcohol

Dowan Kim, Jeyoung Jung, Su-il Park, Jongchul Seo

Department of Packaging, Yonsei University, 1 Yonseidae-gil, Wonju, Gangwon-do 220-710, Korea

Correspondence to: J. Seo (E-mail: jcseo@yonsei.ac.kr)

ABSTRACT: A series of LDPE/PVA blend films were prepared via a twin-screw extruder, and their morphology, thermal property, oxygen and water vapor permeation, surface properties, and mechanical properties were investigated as a function of the PVA content. During the extrusion process of the blend films, glycerin improved the compatibility and processing conditions between LDPE and PVA. The melting temperature (T_m), melting enthalpy (ΔH_m), crystallinity (%), and thermal stability of the thermal decomposition temperature ($T_{5\%}$) of the LDPE/PVA blend films decreased with increasing PVA content. The oxygen permeabilities of the blend films decreased from 24.0 to 11.4 $\text{cm}^3 \cdot \text{cm} (\text{m}^2 \cdot \text{day} \cdot \text{atm})^{-1}$ at 23°C. The WVTR increased from 7.8 to 15.0 $\text{g}(\text{m}^2 \cdot \text{day})^{-1}$ and the water uptake increased from 0.13 to 9.31%, respectively. The mechanical properties of blend films were slightly enhanced up to 2% PVA and then decreased. The physical properties of the blend films strongly varied with the chemical structure and morphology depending on the PVA and glycerin. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41985.

KEYWORDS: applications; blends; composites; packaging

Received 1 October 2014; accepted 11 January 2015

DOI: 10.1002/app.41985

INTRODUCTION

Low-density polyethylene (LDPE) is a synthetic commodity polymer, that is, an extensively used plastic material because of its inexpensive and valuable properties, including mechanical properties, high water resistance, and high chemical resistance.¹ For these reasons, LDPE is widely used in industrial areas such as food, pharmaceutical, and cosmetic industries. However, packaging films composed entirely of LDPE do not have an oxygen barrier property that affects packaging materials and negatively impacts the extensive application.^{2,3} Therefore, LDPE has been used in the form of a multilayer film with EVOH and polyvinyl alcohol (PVA) to overcome this disadvantage of LDPE.^{1,2}

Poly(vinyl alcohol) (PVA) is a special synthetic polymer with multihydroxyl groups.^{4,5} The hydroxyl groups in PVA contribute to strong hydrogen intramolecular and intermolecular bonding, which improve PVA via many excellent properties such as oxygen barrier properties, high mechanical strength, and abrasion resistance.⁴ For these reasons, PVA has an important role in many industrial applications, such as papermaking, textiles, adhesives, and a variety of coatings. However, it is difficult to produce a film using a melting process because the melting temperature and decomposition temperature of PVA are similar.^{5,8} Therefore, most of the production of PVA films is limited to a wet process using water as a solvent, which requires a large

amount of energy consumption, time to dissolve, and drying process.⁶ Additionally, PVA has poor dimensional stability due to high moisture absorption, which restricts its use in many applications. To overcome such problems as the processability and physical properties of PVA film, the study of PVA is widely performed by the addition of inorganic filler such as clay,⁹ graphene oxid,¹⁰ plasticizers^{8,11–14}, and polymer blends.^{1,5,13}

Among the various studies, blends combining two or more polymers have attracted attention to achieve the desired properties.^{1,13,15} Blending is a good way of improving physical properties, such as barrier properties, using a small amount of an expensive polymer like PVA in an inexpensive matrix polymer like LDPE.¹⁴ For a blend, the physical properties may be strongly dependent on the morphology.¹⁵ Specifically, the morphology of the blend is significantly influenced by the results of a complex interplay between the processing conditions and physical and chemical characteristics of the polymer components.¹⁵ For these reasons, plasticizers and coupling agents can be used as additives to improve the compatibility and processing conditions between polymer phases.^{1,13,15} Several studies have investigated the superior physical properties of PVA, including blends of LLDPE/PVA blends,^{1,2} cassava starch/PVA⁹ and PP/PVA.¹³ However, previous investigations have focused on the processing conditions, thermal properties, and mechanical properties of blend films.

Table I. Compositions of the Glycerin-Plasticized LDPE/PVA Blend Films

Sample code (Volume fraction of LDPE : PVA : glycerin)	Compositions			
	LDPE (g)	PVA (g)	Glycerin (g)	Total (g)
Pure LDPE (100 : 0 : 0)	300	0	0	300
LDPE/PVA 2% (97 : 1.5 : 1.5)	294	6	6	306
LDPE/PVA 5% (92.7 : 3.7 : 3.6)	285	15	15	315
LDPE/PVA 10% (85.7 : 7.3 : 7.0)	270	30	30	330
LDPE/PVA 20% (72.8 : 13.9 : 13.3)	240	60	60	360

In this study, the improvement in oxygen barrier property of LDPE could be achieved through the formation of LDPE/PVA blend films. At that time, LDPE was used as a supporting material for the successful melting process of PVA with excellent oxygen barrier and mechanical properties for packaging application. However, blending of PE and PVA has poor compatibility (e.g., phase separation) and processing conditions.⁴ Therefore, it is hypothesized that the addition of glycerin as a plasticizer could improve compatibility and processing conditions due to enhanced thermal characteristics, dispersion and interfacial interaction of PVA into the LDPE matrix for the extrusion system. In addition, the morphological structure, thermal properties, oxygen permeability, and water permeability of LDPE/PVA blend films were thoroughly investigated as a function of PVA content for packaging applications.

EXPERIMENTAL

Materials

Lutene-H[®] ME8000 LDPE resin was provided by LG Chemical Co., Ltd. (Seoul, Korea). LDPE has a MFI of 7.5 g/10 min (ASTM D1238) and a density of 0.918 gcm⁻³. Fully hydrolyzed PVA F-17A (98.0–99.5% degree of hydrolysis, M_w : 74,800 gmol⁻¹) was kindly supplied by OCI Co., Ltd. (Incheon, Korea). For use as a plasticizer of LDPE/PVA blends, glycerin (C₃H₈O₃), a plasticizer of hydrocarbons obtained from petroleum fractions by solvent crystallization, was purchased from Daejung Chemical & Material Co., Ltd. (Siheung, Korea). In this study, all materials were used without further purification.

Preparation of Glycerin-Plasticized LDPE/PVA Blend Films

Using the compositions listed in Table I, PVA and glycerin were mixed in a high-viscosity kneader tester (TO-350, Testone Co., Gwangmyeong, Korea) at 175°C with a rotor speed of 50 rpm for approximately 5 min, and then, LDPE was added at the same conditions. The glycerin-plasticized LDPE/PVA mass was thoroughly oven-dried to minimize the water effect and was pulverized using a grinder (MF 10 basic, IKA Co., Seoul, Korea) to obtain fine granules. Finally, glycerin-plasticized LDPE/PVA blend films were processed using a laboratory-scale twin-screw extruder (BA-19, BauTech Co., Uijeongbu, Korea) with a Φ of 19 and L/D ratio of 40 : 19. The setting temperature of the extruder was 175°C (Header), 175°C (Zones 1–6) and 120°C (Feed Zone). As shown in Figure 1, the transparent and non-sticky blend films were successfully obtained through an extrusion process. The film thickness was maintained at approximately 70 μ m to aid in evaluating the physical properties.

Characterization

To characterize the glycerin-plasticized LDPE/PVA blend films, Fourier transform infrared spectra (FTIR) were recorded on a Spectrum 65 FTIR spectrometer (PerkinElmer Co. Ltd., MA) from 400 to 4000 cm⁻¹ using the attenuated total reflection (ATR) mode. For the morphology of the glycerin-plasticized LDPE/PVA blends films, wide angle X-ray diffraction (WAXD) patterns were obtained using a D/MAX-2500H X-ray diffractometer (Rigaku Co. Ltd., Tokyo, Japan) with a CuK α (α = 1.5406 Å) radiation source. To investigate the miscibility of the glycerin-plasticized LDPE/PVA blend films, SEM images were obtained using the Quanta FEG250 scanning electron microscope (FEI Co. Ltd., Hillsboro, OR). To analyze the fractured surfaces of the glycerin-plasticized LDPE/PVA blend films, the films were first frozen in liquid nitrogen and then broken to produce a cross section. Prior to the examination, all of the samples were coated with a thin layer of platinum (Pt). Thermogravimetric analysis (TGA) was used to determine the thermal stability and decomposition of pure PVA, pure LDPE, and glycerin-plasticized LDPE/PVA blend films. The analysis was performed using a TGA 4000 thermogravimetric analyzer (PerkinElmer Co. Ltd., MA) at a heating rate of 20°Cmin⁻¹ from 50 to 600°C under a nitrogen atmosphere. The thermal properties of pure PVA, pure LDPE, and glycerin-plasticized LDPE/PVA blend films were analyzed using a Q10 differential scanning calorimeter (TA Instrument Co. Ltd., DE) under a



Figure 1. Photograph images of the glycerin-plasticized LDPE/PVA blend films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

nitrogen atmosphere. The samples were heated from -40°C to 240°C at a rate of $10^{\circ}\text{Cmin}^{-1}$. The oxygen transmission rates (OTR) of the glycerin-plasticized LDPE/PVA blend films were measured with an OTR 8001 oxygen permeability tester (Systech Instruments Co. Ltd., IL). The OTR test was performed at 23°C under dry conditions. The oxygen permeability (OP, $\text{cm}^3\cdot\text{cm}(\text{m}^2\cdot\text{day}\cdot\text{atm})^{-1}$) was calculated using eq. (1).

$$OP = \frac{OTR \cdot L}{\Delta p} \quad (1)$$

where OTR is the oxygen transmittance rate of the blend films ($\text{cm}^3\text{m}^{-2}\cdot\text{day}$), L is the film thickness (cm) and Δp is the partial oxygen pressure difference (atm) across the two sides of the blend films.^{15–17}

The water vapor transmission rates (WVTR) of the glycerin-plasticized LDPE/PVA blend films were measured with a WVTR 7001 water vapor permeability tester (Systech Instruments Co. Ltd.). The WVTR tests were performed at 37.8°C and 90% relative humidity. The water uptake for the glycerin-plasticized LDPE/PVA blend films was gravimetrically determined according to ASTM D570-98.^{18,19} Before the test, all samples were completely dried in a vacuum oven at 80°C for 24 h and the weight of the dried samples (W_d) was measured using a microbalance. The dried samples were stored in a humidified chamber with deionized water for 24 h, the excess surface water was removed with moist Kim wipes, and the sample was weighed (W_s). The water uptake (S) was calculated using eq. (2).

$$S(\%) = \frac{W_d - W_s}{W_d} \times 100 \quad (2)$$

The water contact angle on the glycerin-plasticized LDPE/PVA blend films was measured using a Phoenix 300 contact angle goniometer (SEO Co. Ltd., Suwon, Korea). To minimize the effect of water evaporation on the contact angle, all analyses were conducted in a humidity chamber in the controlled range of 80–90% relative humidity. The surface free energies of the glycerin-plasticized LDPE/PVA blend films were estimated via the Owens/Wendt method, utilizing the theory of adhesion work between solid and liquid phases, from which polar (γ^p) and nonpolar or dispersive (γ^d) surface free energies could be derived.^{20,21}

The mechanical properties of the LDPE/PVA blend films were measured using a universal testing machine QM 100T (Qmesys Co. Ltd., Kwangmyeong, Korea) according to ASTM D 638-10.²² The acquisition parameters were as follows: 500 mmmin^{-1} test-speed, 5 kg load cell, 1 cm specimen width, and 8 cm specimen length. The resulting profiles were analyzed using MC tester version 12.6.0 (Qmesys Co. Ltd., Kwangmyeong, Korea).

RESULT AND DISCUSSION

Preparation of the LDPE/PVA Blend Films

FTIR analysis was performed to confirm the changes in the chemical structure and interfacial interactions between LDPE, PVA, and glycerin.^{1,5,13,23} Figure 2 shows the FTIR spectra of the glycerin, pure PVA, pure LDPE, and LDPE/PVA blend films. Glycerin exhibited characteristic absorption peaks of $3000\text{--}3600\text{ cm}^{-1}$, which are caused by —OH— stretching and vibration. Furthermore, the absorption peaks at approximately 2875

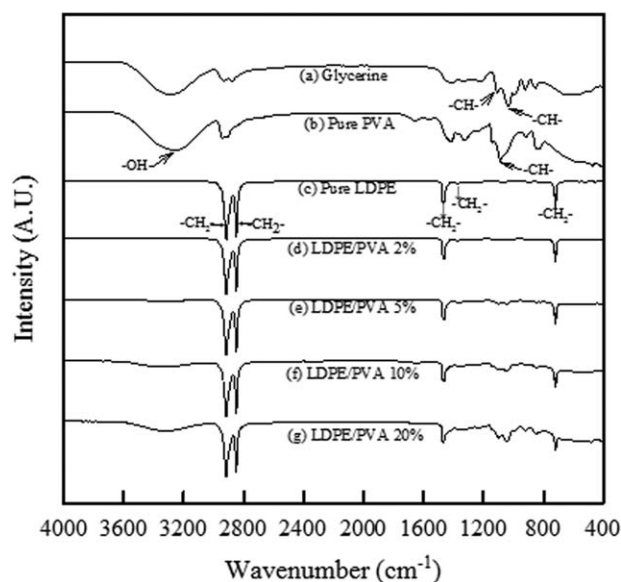


Figure 2. FTIR spectra of glycerin, pure PVA, pure LDPE, and LDPE/PVA blend films.

and 2927 cm^{-1} belong to the symmetric and stretching vibration of $\text{—CH}_2\text{—}$, whereas the peaks at 1119 and 1030 cm^{-1} are due to the wagging vibration of —CH— .¹² Pure PVA exhibited characteristic absorption peaks at 2956 , 2919 , and 2852 cm^{-1} , which are caused by the $\text{—CH}_2\text{—}$ asymmetric stretching vibration band. Broad characteristic peaks appeared near $3000\text{--}3600\text{ cm}^{-1}$ in the PVA spectra, corresponding to —OH— stretching vibrations. The absorbance peak at 1087 cm^{-1} is due to —C—O— .^{12,23} Pure LDPE exhibited characteristic absorption peaks at 2919 and 2852 cm^{-1} , which are caused by the $\text{—CH}_2\text{—}$ asymmetric stretching vibration band. Furthermore, the blend films exhibited the absorption bands near 1475 and 1372 cm^{-1} ,

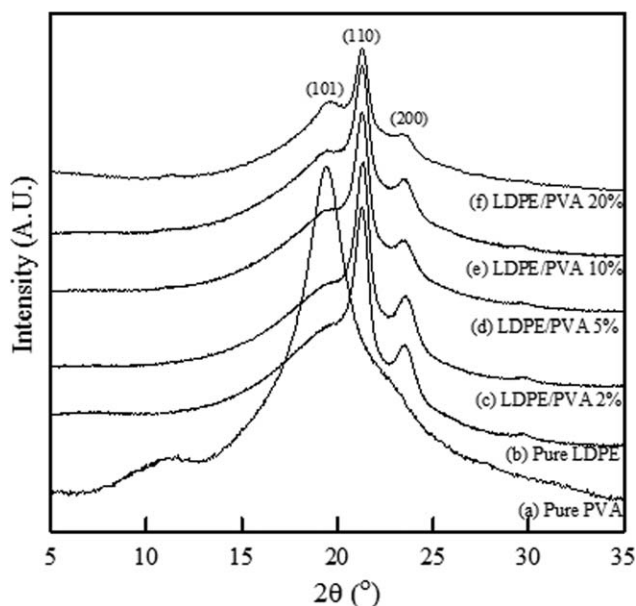


Figure 3. WAXD patterns of pure PVA, pure LDPE, and LDPE/PVA blend films.

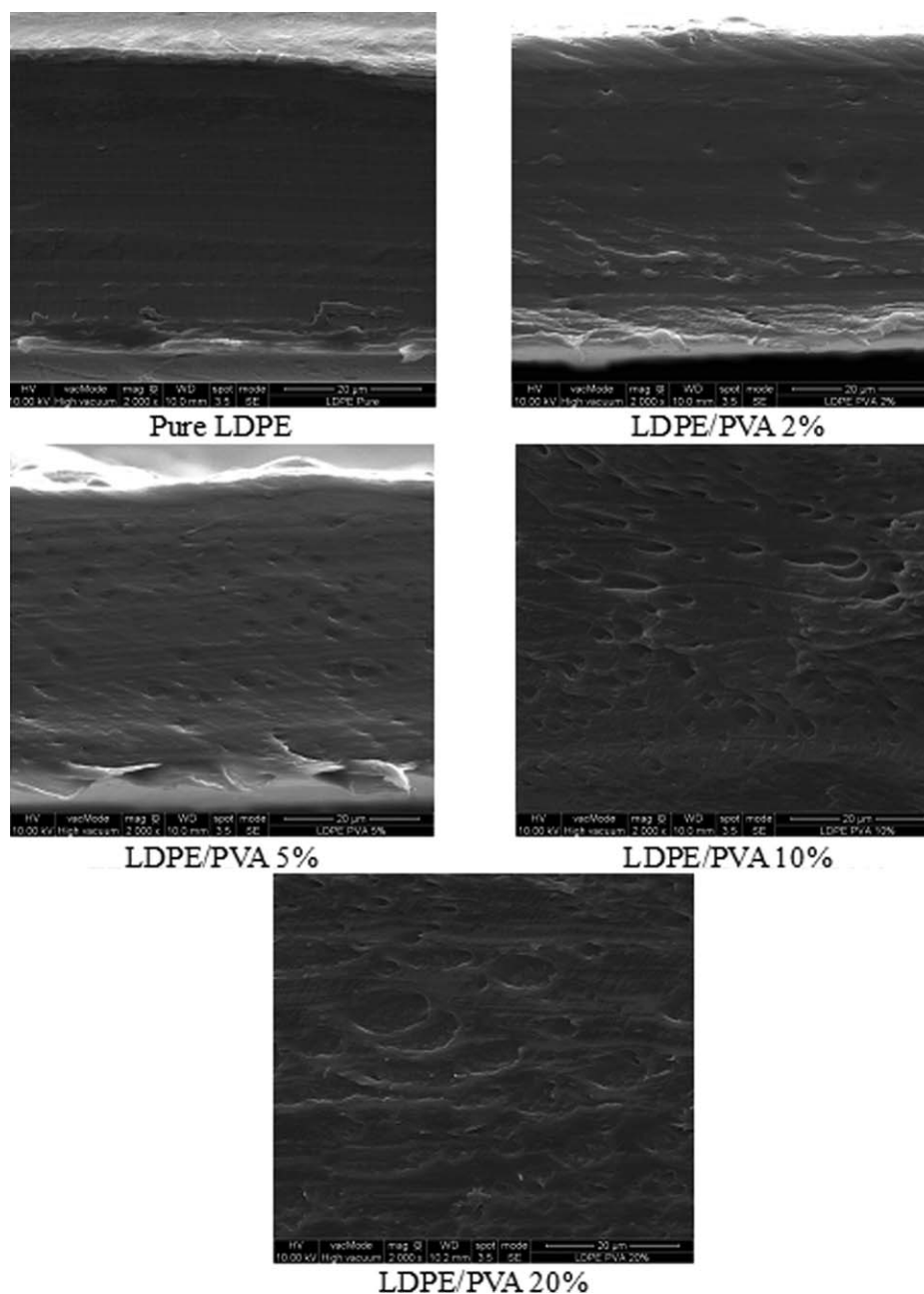


Figure 4. SEM images of the fractured surfaces of the LDPE/PVA blend films.

corresponding to the bending, symmetric deformation, and rocking vibration of $-\text{CH}_2-$. The peaks at 731 and 719 cm^{-1} are due to the in-plane rocking vibration of $-\text{CH}_2-$.²⁴ The intensity of the broad absorption bands between 1037 and 1104 cm^{-1} gradually increased with the PVA and glycerin content in the blend films. The intensity of the $\text{OH}-$ stretching vibration of the LDPE/PVA blend films increased with increasing pure PVA and glycerin contents. The hydrophilicity of LDPE/PVA blend films slightly increased with the intermolecular bonding of $-\text{OH}$ groups between PVA and glycerin and by intramolecular bonding of PVA and glycerin. From these results, the blend films may become more hydrophilic than pure LDPE.¹²

Morphological Structure

The blend morphology is an important characteristic because it may affect the physical properties such as thermal stability and permeability properties.^{5,12,13} The morphology of the plasticized LDPE/PVA blend films is widely characterized by WAXD and SEM experiments.^{5,12,13} Figure 3a shows the WAXD patterns of pure PVA. The pure PVA showed a strong diffraction peak at $2\theta = 19.6^\circ$ ((101) plane), corresponding to a mean intermolecular distance of 4.53 \AA .²⁵ Pure LDPE has a broad amorphous halo in the range of $15\text{--}25^\circ$ (2θ), as well as two sharp diffraction peaks at $2\theta = 21.33^\circ$ ((110) plane) and 23.74° ((200) plane). As the PVA and glycerin content increased from 0 to 20%, the intensity of diffraction peaks (101)

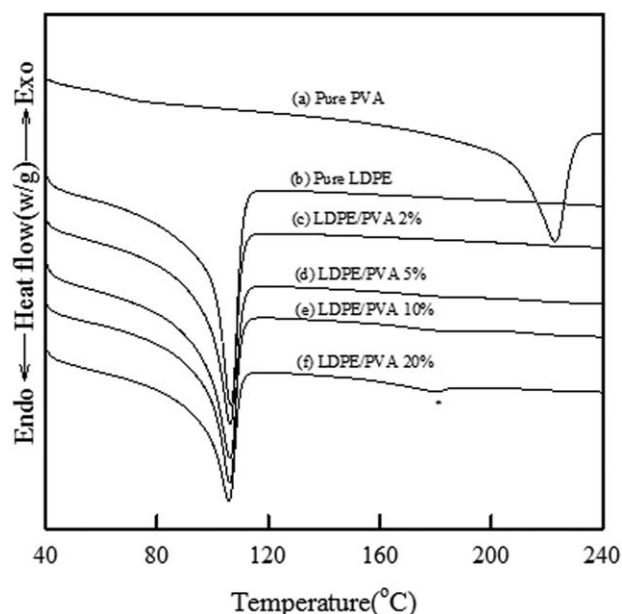


Figure 5. DSC thermograms of pure PVA and LDPE/PVA blend films.

originating from PVA increased; however, the intensity of the (110) and (200) diffraction peaks originating from pure LDPE decreased and the amorphous halo decreased. PVA with a semi-crystalline structure may improve the crystallinity of the LDPE matrix by decreasing the mobility of the LDPE chains near the PVA surface. However, regardless of the PVA content, the crystallinity of blend films decreased via the addition of PVA and glycerin. The —OH group of glycerin interacts with the —OH group of PVA, which prevents the formation of the crystalline region in the PVA and LDPE matrix.^{6,12}

As shown in Figure 4, SEM analysis for the fractured surfaces was performed to determine the miscibility of PVA in the LDPE matrix. Pure LDPE showed a relatively smooth fracture surface.²⁶ As shown in Figures 4(b–d), the fractured surface of the LDPE/PVA blend films with glycerin exhibited an interconnected smooth fractured surface. This finding may suggest that glycerin provides good adhesion and interaction between the nonpolar LDPE and polar PVA. However, the blend film with relatively high PVA content (5–20%) in the LDPE matrix exhibited some voids and showed a slight phase separation of LDPE

and PVA. Therefore, it may have adversely affected their mechanical properties, which may relate to the low interfacial interaction between LDPE and PVA.

Thermal Properties

To investigate how the PVA and glycerin content affects the thermal stability of LDPE/PVA blend films, DSC and TGA analyses were performed in a nitrogen atmosphere. As shown in Figure 5, the DSC curve of pure LDPE presents an endothermic peak at 107.3°C corresponding to the melting of pure LDPE. This endothermic peak slightly shifted to a lower temperature as the PVA content increased. This may result from the polymer matrix becoming less dense and increased chain mobility of LDPE with the addition of PVA and glycerin.²⁷ In addition, with increasing PVA contents in LDPE/PVA blend films, the new endothermic peak appeared near 160–200°C, which may be due to the existence of a new polymer crystalline phase in LDPE matrix, induced by the presence of the PVA. The melting enthalpy (ΔH_{m1}) originating from pure LDPE and the melting enthalpy (ΔH_{m2}) from new crystalline phase by PVA were separately calculated and summarized in Table II.

The degree of crystallinity (%) of the LDPE/PVA blend film was calculated using eq. (3).

$$\% \text{Crystallinity} = \Delta H_m / \Delta H_m^0 \times 100 \quad (3)$$

where ΔH_m is the melting enthalpy of the blend films and ΔH_m^0 is the melting enthalpy for the 100% crystalline LDPE sample (293 Jg^{-1}).^{28,29} The calculated crystallinity of the LDPE/PVA blend films decreased from 47.1 to 27.2%, likely due to the addition of PVA and glycerin. The incomplete miscibility and ratio of components between LDPE, PVA, and glycerin is a possible explanation for these results.⁷ The chain arrangement of PVA in the LDPE matrix was disturbed, and crystalline regions were prevented by immiscibility and steric hindrance, which decrease the melting temperature, melting enthalpy, and % crystallinity to a certain degree.^{1,7} This result is in agreement with the WAXD results.

As shown in Figure 6 and Table II, the degradation patterns and thermal stability are dependent on the content of PVA and glycerin. Pure LDPE showed one-step degradation. However, all the LDPE/PVA blend films exhibited a three-step degradation process with the addition of different PVA and glycerin contents. The three-step process indicates that the existence of PVA and glycerin significantly influences the thermal degradation patterns of the LDPE/PVA blend

Table II. DSC Results of the LDPE/PVA Blend Films

Sample code	DSC					
	T_{m1} (°C) ^a	ΔH_{m1} (Jg ⁻¹) ^a	T_{m1} (°C) ^b	ΔH_{m2} (Jg ⁻¹) ^b	ΔH_{mt} (Jg ⁻¹) ^c	Crystallinity (%) ^d
Pure LDPE	107.3	138.0	–	–	138.0	47.1
LDPE/PVA 2%	107.3	133.8	–	–	133.8	45.7
LDPE/PVA 5%	107.1	123.6	–	–	123.6	42.2
LDPE/PVA 10%	107.5	94.2	180.3	2.0	96.2	32.8
LDPE/PVA 20%	106.9	75.6	179.1	4.2	79.8	27.2

^aMelting temperature and enthalpy of LDPE fraction in LDPE/PVA blend films.

^bMelting temperature and enthalpy of PVA-induced new crystallites in LDPE/PVA blend films.

^cTotal melting enthalpy of the LDPE/PVA blend films.

^d% Total crystallinity of the LDPE/PVA blend films.

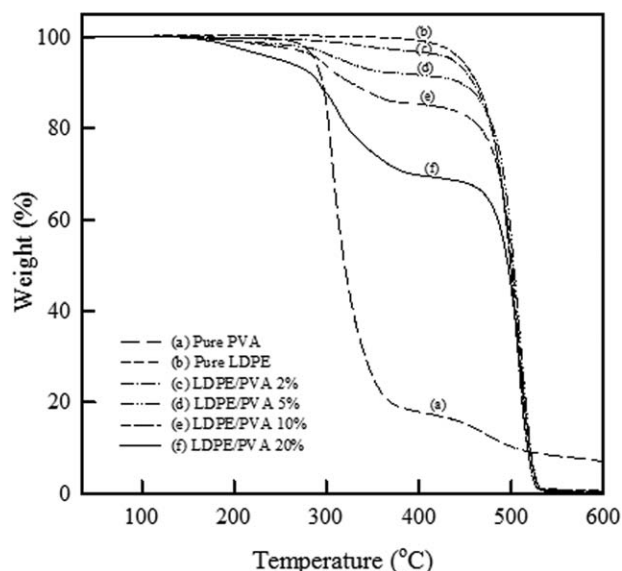


Figure 6. TGA curves of pure PVA and LDPE/PVA blend films.

films. The pure LDPE showed one degradation stage between 400 and 530°C, which was due to the chain scission of the carbon-carbon bond in the main chain.^{5,12} However, by adding PVA and glycerin, the LDPE/PVA blend films showed a three-step degradation. The first degradation stage, between 150 and 300°C, was due to the decomposition of the hydroxyl group in PVA and glycerin.⁵ The second (300–400°C) and third decomposition (400–530°C) stages indicate the existence of a chemical degradation process resulting from bond scission (carbon-carbon bonds) in pure PVA and pure LDPE, which is characteristic of immiscible polymer blends.¹²

Oxygen Permeability

In general, the barrier properties of polymer are affected by several factors such as crystallinity and orientation, chemical interactions between the polymer and permeant, and chemical structure

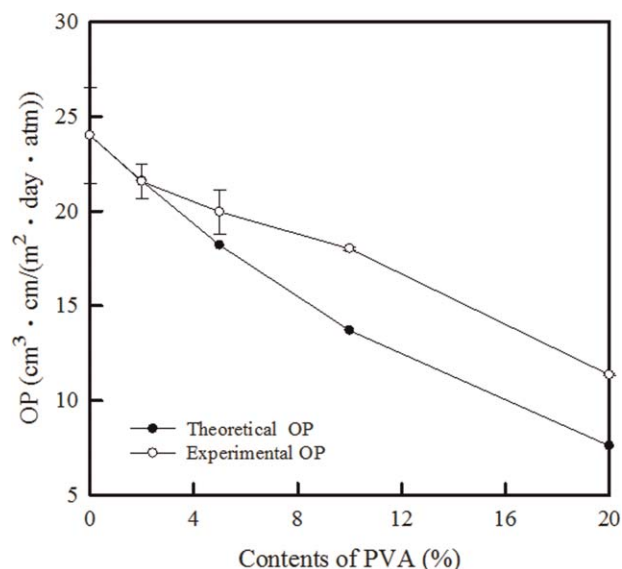


Figure 7. OPs of the LDPE/PVA blend films.

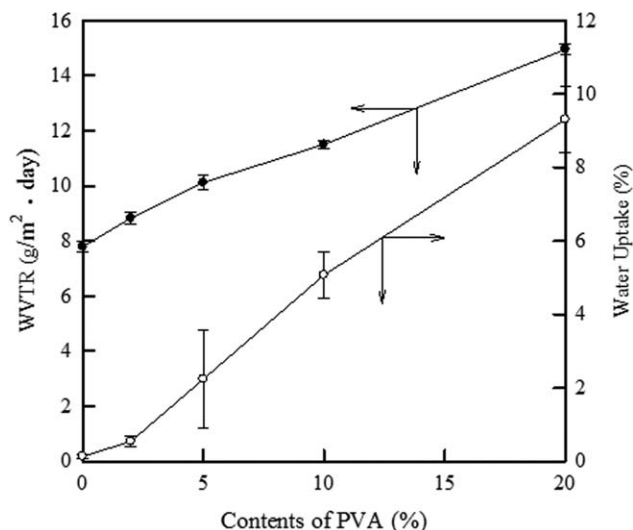


Figure 8. WVTRs and water uptake of the LDPE/PVA blend films.

including their polarity, stereoregularity of polymer.¹⁶ Although LDPE, HDPE, and LLDPE have the same chemical structure of $-(CH_2-CH_2)_n-$, they have different barrier properties due to different density, MW, and MWD.³⁰ References 30 and 31 exhibited that OP values of LDPE and HDPE films are 16.3 ~ 21.3 and 4.0 ~ 7.3 $cm^3 \cdot cm / (m^2 \cdot day \cdot atm)^{-1}$, respectively.^{30,31} Furthermore, as described in several literatures,^{13,16,32-34} the permeabilities of blends or nanocomposite films are strongly dependent on the morphological and chemical structures. Of the LDPE-based nanocomposite films, LDPE/KMnO₄ showed in the range of 21.7 ~ 24.8 $cm^3 \cdot cm / (m^2 \cdot day \cdot atm)^{-1}$ and LDPE/nano-CaCO₃ did in the range of 9.67 $cm^3 \cdot cm / (m^2 \cdot day \cdot atm)^{-1}$.^{32,33} Furthermore, the OP value of LDPE/starch blend films varied from 71.25 to 337.5 $cm^3 \cdot cm / (m^2 \cdot day \cdot atm)^{-1}$ depending on the starch content.³⁴

As shown in Figure 7, the OP value of pure LDPE is 24.0 $cm^3 \cdot cm / (m^2 \cdot day \cdot atm)^{-1}$ at 23°C, and the LDPE/PVA blend films varied from 21.6 to 11.4 $cm^3 \cdot cm / (m^2 \cdot day \cdot atm)^{-1}$. The OP value of the blend films incorporating 2%, 5%, 10%, and 20%

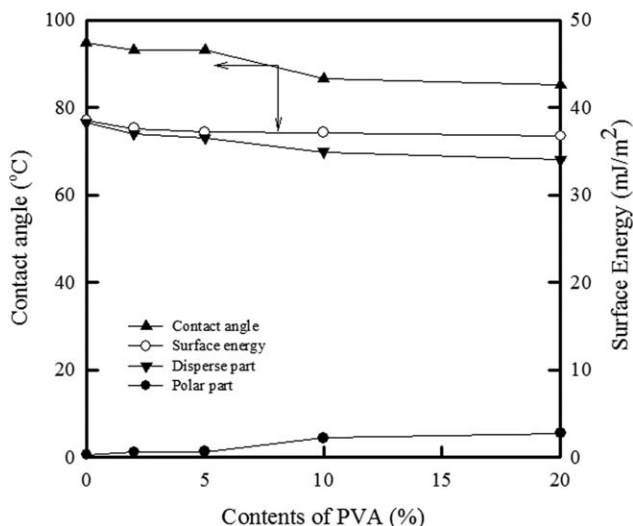


Figure 9. Contact and surface energies of the LDPE/PVA blend films.

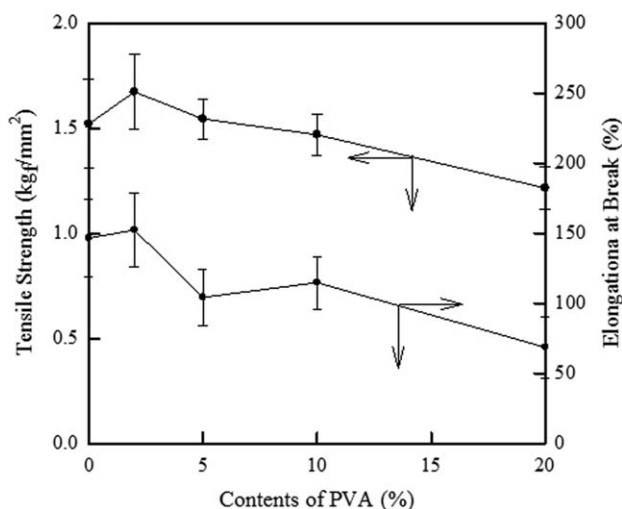


Figure 10. Tensile strength and elongation at break of the LDPE/PVA blend films.

of PVA contents were greatly decreased by 10.2%, 16.9%, 24.9%, and 52.7%, respectively. Comparing other researches, our blend films are more effective in enhancing oxygen barrier property of pure LDPE.^{32,34,35}

In general, nonpolar LDPE with a flexible chain has a high degree of chain branching, which results in disrupted chain packing and low crystallinity.^{13,15–17} For these reasons, the oxygen gas is easily permeated in the LDPE matrix. However, the addition of PVA with a polar group, such as —OH , and the high packing density in LDPE may provide much better oxygen barrier properties due to the weak interaction between PVA and oxygen.^{13,16} The experimental OP in LDPE/PVA blend films are enhanced with the PVA content, though it is greater than the theoretical value, as given in eq. (4).

$$\log OP_{\text{blend}} = \Phi_1 \log OP_{\text{LDPE}} + \Phi_2 \log OP_{\text{PVA}} \quad (4)$$

where OP_{blend} is the oxygen permeability of blend films, Φ_1 and Φ_2 are the volume fractions of LDPE and PVA in blend films, respectively, and OP_{LDPE} and OP_{PVA} are the oxygen permeability of LDPE and PVA.^{15–17} This deviation may be due to the miscibility of the LDPE and PVA components and the morphology of blend films. For a small amount of PVA and glycerin (2%), glycerin may improve the miscibility between nonpolar LDPE and polar PVA, thus allowing for decreasing oxygen permeability through the blend films that is the same as the theoretical OP value. However, as indicated by SEM and WAXD analyses, a weak interfacial interaction and small voids exist in blend films with high PVA content, which may not effectively decrease the oxygen permeabilities of blend films. Furthermore, the same amount of glycerin in blend films is increased with PVA contents. The increase of glycerin may contribute to less dense structural regularity in blend films, which negatively affects to decrease the experimental OP values. Resultantly, large difference results in between theoretical OP and experimental OP values.

Water Vapor Permeability

As shown in Figure 8, the WVTR and water uptake results were different from the OTR results. With increasing PVA content, the WVTR and water uptake values of the LDPE/PVA blend films

increased from 7.8 to 15.0 $\text{g}(\text{m}^2 \text{day})^{-1}$ at 37.8°C and from 0.13 to 9.31% as the PVA content increased. This indicates that the water absorbency of LDPE was greatly enhanced by the LDPE/PVA blend systems and the moisture diffusion in the pure LDPE film was increased by the incorporation of PVA with a high affinity for water. Water sorption, diffusion, permeability, and sorption are strongly dependent on the chemical structure of the polymer matrix.^{13,16} In terms of the chemical structure, the degree of hydrophilicity of a surface is a significant factor for water vapor permeability. Specifically, the water affinity of PVA consisting largely of —OH groups is better than that of the LDPE matrix with relatively hydrophobic aliphatic repeat units. It is anticipated that the addition of PVA will increase the hydrophilicity in LDPE. At the same time, the increased water affinity in LDPE/PVA blend films will be more pronounced because the blend films are increasingly swelled and plasticized by the absorbed water, resulting in an increase in WVTR and water sorption.^{13,16} This result coincides with the water contact angles of the pure PVA and LDPE/PVA blend films, as shown in Figure 9. The water contact angles for the pure PVA were measured at 20°. The water contact angles of the LDPE/PVA blend films decreased from 94.8° to 85.2° at a PVA loading up to 20%. This indicates that the hydrophilicity of pure LDPE increases as the relatively hydrophilic PVA content increases. The surface free energy of pure PVA and LDPE/PVA blend films was calculated by the Owens–Wendt method, utilizing the contact-angle measurements of deionized water and diiodomethane.^{20,21} The total surface free energies are the sum of the polar and disperse parts. As shown in Figure 9, the surface energies of the polar and disperse parts in pure PVA were 34.98 and 36.48 mJm^{-2} , respectively, which indicates that pure PVA has a polar group originating from the —OH group. As shown in Figure 9, the surface energy of the polar part in the LDPE/PVA blend films slightly increased due to the polar structure of PVA. It is anticipated that —OH groups will form during blending of LDPE and PVA, which will induce relatively hydrophilic surfaces in the blend films. Based on these results, water vapor will easily interact with the polar hydroxyl groups of the blend films and weaken strong intermolecular interactions, thereby facilitating segmental motion, water sorption, and diffusion.

Mechanical Properties

The mechanical properties of pure LDPE and four different LDPE/PVA blend films were investigated using a universal testing machine, and their results are depicted in Figure 10. The tensile strength and elongation at break of pure LDPE were 1.52 $\text{kg} \cdot \text{mm}^{-2}$ and 146.45%, respectively. Depending on the PVA and glycerin, it slightly increased its maximum value at 2% PVA loading in LDPE and then decreased thereafter. For small PVA and glycerin contents, glycerin may improve the PVA dispersion and enhance the interaction between nonpolar LDPE and polar PVA.⁵ However, when the content of PVA and glycerin is greater than a certain value, they cannot be uniformly dispersed in the blend or adhered between the LDPE and PVA with different polarities, which induces a reduction in mechanical properties of the blend films with high PVA and glycerin content. Additionally, as indicated by SEM, the increasing small void makes the bond matrix discontinuous and leads to catastrophic failure of the LDPE/PVA blend films (5–20%).^{5,36} Further studies on the enhancement of

interfacial interactions between LDPE and PVA are required to improve the mechanical properties.⁵

CONCLUSIONS

LDPE/PVA blend films were successfully prepared through an extrusion process, which were used as a packaging material with improved oxygen permeability, mechanical properties, and processability, and their physical properties were investigated by the effect of PVA and glycerin content. The physical properties of blend films strongly varied with the chemical structure and morphology depending on the PVA and glycerin. PVA and glycerin incorporation caused the WVTR to increase from 7.8 to 15.0 g(m² day)⁻¹ at 37.8°C, and the water uptake increased from 0.13 to 9.31%. The chemical structure of glycerin-plasticized LDPE/PVA blend films may become more hydrophilic than pure LDPE. Therefore, the water vapor easily interacted with polar hydroxyl groups of the blend films and then absorbed and diffused into the blend films. However, the oxygen permeability of LDPE/PVA blend films decreased from 24.0 to 11.4 cm³·cm (m² day atm)⁻¹ at 23°C with the incorporation of PVA. The mechanical properties of blend films slightly exceeded the maximum value at 2% PVA loading in LDPE and then decreased thereafter, which may be related to the good miscibility and interfacial interaction of the glycerin-plasticized LDPE/PVA blend films at low PVA content. However, a small amount of voids and phase separation were observed in blend films with relatively high PVA and glycerin loading. Although the compatibility and processability of mixed polymers needs to be improved to maximize the performance of LDPE-/PVA-blend films, enhanced oxygen barrier and mechanical properties of LDPE/PVA blend films make them potential candidates for packaging materials to prevent lipid oxidation in low-moisture food, including powdered beverages, chocolate, nuts, and ready-to-eat cereal.

ACKNOWLEDGMENTS

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2013R1A1A2057674).

REFERENCES

1. Nordin, R.; Ismail, H.; Ahmad, Z.; Rashid, A. *J. Vinyl. Addit. Technol.* **2012**, *18*, 120.
2. Piringer, O. G.; Baner, A. L. *Plastic Packaging, Plastic Packaging*; Wiley: Weinheim, **2008**.
3. Minkova, L.; Yordanov, H.; Filippi, S. *Polymer* **2012**, *43*, 6195.
4. Cheng, N.; Li, L.; Wang, Q. *Plast. Rubber. Compos.* **2007**, *36*, 283.
5. Ismail, H.; Nordin, R.; Ahmad, Z.; Rashid, A. *Iran. Polym. J.* **2010**, *19*, 297.
6. Jang, J.; Lee, D. K. *Polymer* **2003**, *44*, 8139.
7. Yang, C.; Lee, Y. *Thin Solid Films* **2009**, *517*, 4735.
8. Kim, H. M.; Lee, J. K.; Lee, H. S. *Thin Solid Films* **2011**, *519*, 7766.
9. Rahman, W. A. W. A.; Sin, L. T.; Rahmat, A. R.; Samad, A. A. *Carbohydr. Polym.* **2010**, *81*, 805.
10. Alexy, P.; Kachova, D.; Krsiak, M.; Bakos, D.; Simkova, B. *Polym. Degrad. Stab.* **2002**, *78*, 413.
11. Wenqian, W.; Tian, H.; Xiang, A. *J. Polym. Environ.* **2012**, *20*, 63.
12. Sreekumar, P. A.; Al-Harathi, M. A.; De, S. K. *J. Appl. Polym. Sci.* **2012**, *123*, 135.
13. Jang, J.; Lee, D. K. *Polymer* **2004**, *45*, 1599.
14. Lange, J.; Wyser, Y. *Packag. Technol. Sci.* **2003**, *16*, 149.
15. George, S. C.; Ninan, K. N.; Thomas, S. *Eur. Polym. J.* **2001**, *37*, 183.
16. Solovyov, S.; Goldman, A. *Mass Transport & Reactive Barriers in Packaging*; Destech Publications, Inc: Pennsylvania, **2008**.
17. Wang, Y.; Allan, J.; Easteal, X.; Chen, D. *Packag. Technol. Sci.* **1998**, *11*, 169.
18. American Society for Testing and Materials, ASTM D570-98. In: *Annual Book of ASTM Standards*, West Conshohocken: PA, **2002**.
19. Lee, Y.; Kim, D.; Seo, J.; Han, H.; Khan, S. B. *Polym. Int.* **2013**, *62*, 1386.
20. Ataefard, M.; Moradian, S.; Mirabedini, M.; Ebrahimi, M.; Asiaban, S. *Plasma Chem. Plasma Process.* **2008**, *28*, 377.
21. Ataefard, M.; Moradian, S. *Appl. Surf. Sci.* **2011**, *257*, 2320.
22. American Society for Testing and Materials, ASTM D638-10. In: *Annual Book of ASTM Standards*, West Conshohocken: PA, **2002**.
23. Mansur, H. S.; Sadahira, C. M.; Souza, A. N.; Mansur, A. A. *P. Mater. Science. Eng. C* **2008**, *28*, 539.
24. Kim, D.; Kim, I.; Seo, J.; Seo, J. *App. Chem. Eng.* **2012**, *23*, 546.
25. Hu, W. W.; Zhang, X. H.; Zhang, Q. Z.; Liu, Q. L.; Zhu, A. M. *J. Appl. Polym. Sci.* **2012**, *126*, 778.
26. Wang, J.; Xu, C.; Hu, H.; Wan, L.; Chen, R.; Zheng, H.; Liu, F.; Zhang, M.; Shang, X.; Wang, X. *J. Nanopart. Res.* **2012**, *13*, 869.
27. Souza, A. C.; Benze, R.; Ferrao, E. S.; Ditchfield, C.; Coelho, A. C. V.; Tadini, C. C. *LWT-Food Sci. Technol.* **2012**, *46*, 110.
28. Alkan, C.; Günther, E.; Hiebler, S.; Ensari, Ö. F.; Kahraman, D. *Sol. Energ.* **2012**, *86*, 1761.
29. Hameed, T.; Hussein, I. A. *Polymer* **2002**, *43*, 6911.
30. Seike, S. E. M.; Culter, J. D.; Hernandez, R. J. *Plastics Packaging*; Hanser: Ohio, **2004**.
31. Walker, A. M.; Tao, Y.; Torkelson, J. M. *Polymer* **2007**, *48*, 1066.
32. Khosravi, R.; Hashemi, S. A.; Sabet, S. A.; Rezadoust, A. M. *Polym-Plast Technol.* **2013**, *52*, 126.
33. Luo, Z.; Wang, Y.; Wang, H.; Feng, S. *J. Sci. Food Agr.* **2014**, *94*, 3273.
34. Baldev, R.; Udaya, S. K.; Siddaramaiah, *Adv. Polym. Technol.* **2004**, *23*, 32.
35. Barden, L.; Decker, E. A. *Crit. Rev. Food. Sci. Nutr.* **2013**, Online version.
36. Kim, D.; Jang, M.; Seo, J.; Nam, K. H.; Han, H.; Khan, S. B. *Compos. Sci. Technol.* **2013**, *75*, 84.