Effect of porous zeolite on temperature-dependent physical properties of polypropylene/octadecane (PP/OD) composite films

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Abstract. Polymeric materials with temperature-dependent gas permeabilities using a phase change material are designed and their applicability as a packaging system investigated. Polypropylene/octadecane/zeolite (PP/OD/ZL) composite films were prepared *via* extrusion process. ZL was used as a filler to enhance the dispersion and interfacial interaction between the OD and the PP originating from different flowabilities during the extrusion process. (FTIR) and (WAXD) analyses showed that the incorporation of ZL increased the interfacial interaction between PP and OD, resultantly enhancing the thermal stability, mechanical properties, and the oxygen transmittance rate and mechanical properties after contact with food simulants and thermal treatment. When the temperature was elevated from 10 to 30 °C, oxygen and water vapor transmittance rate of the composite films increased sharply because of the influence of the OD content. It was surmised that temperature-dependent permeation jump caused by increasing of segmental mobility of OD phase and converting the crystalline structure to an amorphous one of OD phase in the composite films. However, the permeation jump in the composite films was weakened as the ZL content increased. These results are related to changes in the interfacial interaction and crystallinity in the composite films due to the addition of ZL.

Keywords: polymer composites, temperature-dependent permeabilities, physical properties, packaging applications

1. Introduction

Gas permeation through polymers occurs *via* a sorption-diffusion mechanism [1–5]. Various penetrants such as O₂ and water vapors adsorb onto the upper surface of a polymer, diffuse through the polymer matrix, and desorb from the opposite surface, while gas permeation properties of a material are strongly dependent on its chemical structure and changes in the polymer morphology originating from the temperature variations [1–3, 5]. During the last several decades, many different groups have conducted research studies on the permeability of various pene-

trant molecules (such as O₂ and water vapors) in polymers [3–5]. Among the studied materials, polymers characterized by temperature-dependent gas and water vapor permeability properties such as poly(alkyl acrylate) [3, 5], poly(*N*-isopropylacrylamide) [1], polyurethane [6, 7], low-density polyethylene/paraffin wax (LDPE/PW) composite films [2], and polypropylene/octadecane (PP/OD) composite films [8] are becoming increasingly important in packaging applications for agricultural products and medical devices. The quality of agricultural products strongly depends on atmospheric composi-

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tions, which are affected by variations of respiration rates, transpiration during storage, and distribution environments [1, 3, 5]. Thus, sterilization of medical devices is required to maintain their aseptic environments until they are ready to use, and their packaging materials must possess the ability to survive a sterilization process [9]. Therefore, chemical and physical properties of the packaging materials should be adjusted to provide optimal gas permeability properties for practical applications in various fields.

Phase change materials (PCMs) are materials that store and release heat energy during temperature-driven phase changes [2, 8, 10–12]. Among various PCMs, PW is readily available and possess desirable characteristics such as large latent heat storage capacity, chemical inertness and stability, and non-toxicity [2, 10–13]. For these reasons, PW-based materials have been investigated for energy storage applications and thermal protection systems [10–12]. Various research groups have studied polymer/PCM composites because of their ability to maintain shape stability during usage [2, 8, 10, 11]. The polymer matrix is able to arrange PCM species in a compact form and minimize PCM leakage from the polymer even after melting. However, some issues related to the polymer/PCM composites still persist including PCM leakage from the polymer matrix at high PCM contents and poor thermal conductivity. To overcome these problems, some researchers modified the known polymer/PCM composites by adding inorganic fillers [10, 11]. Mhike *et al.* [10] investigated LDPE/soft Fisher-Tropsch wax/graphite composite sheets prepared by compounding and hot press methods. Molefi *et al.* [11] studied LDPE/wax/Cu, linear low-density polyethylene (LLDPE)/wax/Cu, and high-density polyethylene (HDPE)/wax/Cu mixtures prepared by compounding and hot press methods. They found that the incorporated fillers apparently improved thermal stability, thermal conductivity, and mechanical properties of the manufactured polymer/PCM composites for thermal energy storage and thermal protection applications [10, 11].

In our previous researches, polymer/PCM composite films such as LDPE/PW and PP/OD composites were fabricated for food packaging and medical device packaging and sterilization applications, and their temperature-dependent permeation properties were explored as functions of the PCM content and temperature [2, 8]. The melting temperature of PW varies from 5.5 to 90 °C depending on the number of C

atoms (C14–C50) in the chain, which can possibly allow the development of composite films with optimal gas permeability values relying in different operational temperature ranges. The studied composite films contained two different phases (the polymer and PCM ones), and the resulting transformation of the PCM species into a polymer matrix occurring near the PCM phase temperature can significantly affect the morphology of the entire polymer/PCM composite and effectively create passing channels for various penetrants in the polymer matrix [2, 8]. However, it is difficult to uniformly disperse PCM molecules in a polymer matrix during extrusion due to different flowabilities of the polymer and PCM species originating from the corresponding difference in their molecular weights [2, 8]. In addition, it is not sufficient to maintain strong interfacial interactions between the olefin polymers (such as PE and PP) and the PCM species, although the olefin polymers and PW have the same chemical structure, and their composite films form a continuous phase, which results in decreased thermal stability and deterioration of the film mechanical properties [2, 8].

To overcome these disadvantages of the polymer/PCM composite films, the incorporation of porous inorganic materials may synergistically allow the flowability control and enhancement of interfacial interactions due to the penetration of the OD and PP species inside the pores during extrusion. In this study, we have used hydrophobic ZSM-5 zeolite (ZL) as filler for the PP/OD composite films since the PP and OD molecular chains can be accommodated inside the porous structure of ZL. In addition, the hydrophobic ZL is non-polar [14], which can effectively enhance its physical interaction with non-polar OD and PP molecules, resulting in improvement of composite film physical properties. Morphological structures, thermal properties, permeability values, and mechanical properties of the fabricated PP/OD/ZL composite films were thoroughly investigated as functions of the ZL content and temperature. To utilize the as-prepared composite films in food and medical device packaging and sterilization applications, it is critical to evaluate changes in stability, compatibility, and physical properties of the composite films caused by their exposure to high temperatures and different kinds of food [15, 16]. For this purpose, we have evaluated O₂ permeability values and mechanical properties of the composite films after their contact with various food simulants and thermal treatment

according to the standards specified by Regulation (EC) No 1935/2004 [17] and Regulation (EU) No 10/2011 [18].

2. Experiments

2.1. Materials

Homo PP resin was provided by Samsung Chemical Co., Ltd. (Seoul, Korea). It was characterized by a melt flow index of 1.5 g/10 min (ASTM D1238), molecular weight of 250 000–300 000 g/mol, and density of 0.90 g/cm³. As a PCM, OD with a density of 0.78 g/cm³ and melting point of 26–29 °C was purchased from Sigma Aldrich Co., Ltd. (Yongin, Korea). To enhance the dispersion and miscibility of organic PP and inorganic ZL, Fusabond® E588, a maleic anhydride-grafted-polyolefin compatibilizer, was purchased from Dupont Co. Ltd. (Seoul, Korea). As a porous filler, ZL (Hisiv3000) was acquired from Union Showa K.K. Co., Ltd. (Tokyo, Japan). As shown in Figure 1, the Brunauer–Emmett–Teller (BET) surface area and total pore volume of ZL are

385.0 m²/g and 0.2 cm³/g, respectively. The ZL has a hexagonal plate-like crystal structure with its size in the range of 0.6 to 4.3 μm. According to the energy dispersive X-ray spectroscopy (EDAX) elemental analysis, the Si/Al ratio in the obtained samples is 151.

2.2. Preparation of PP/OD/ZL composite films

To remove residual volatile gases such as water vapor and residual compounds from the pores, ZL was first calcined in a muffle furnace at 300 °C for 1 h. Liquid OD obtained by heating the corresponding solid raw material to its melting temperature was mixed with the porous, layered structured ZL. According to the compositions listed in Table 1, six different compositions of the PP/OD/ZL composite pellets were prepared using a twin-screw extruder (BA-19, BauTech Co., Uijeongbu, Korea) for homogeneous mixing and dispersion. To remove water from the obtained pellets, the latter were dried at 80 °C for 12 h. From the as-prepared pellets, six different PP/OD/ZL composite films were prepared using the same extruder. The extruder temperature was set to 19 °C for the header, 190 °C for zones 1–6, and 120 °C for the feed zone. The thickness of the composite films was maintained uniform at approximately 65±2 μm.

3. Characterization

3.1. Morphology

Adsorption-desorption properties were determined to analyze the BET specific surface area and total pore volume of ZL. N₂ adsorption was studied using an ASAP 2010 Instrument (Micromeritics Co. Ltd., Norcross, GA, USA). To identify the dispersion of ZL and interfacial interaction between PP and ZL and ZL and OD in the PP/OD/ZL composite films, fractured scanning electron microscopy (SEM) images were obtained from a Quanta FEG250 scanning

Figure 1. BET, SEM, and EDAX analyses of the hydrophobic ZSM-5 zeolite (ZL).

Table 1. Compositions of the PP/OD composite films containing hydrophobic zeolites.

Sample code	Compositions (weight) [g]				Compositions (volume) [cm ³]			
	PP	E588*	OD	ZL	PP	E588*	OD	ZL
PP/OD/ZL 0%	97	3	20	0	78.8	2.5	18.7	0.0
PP/OD/ZL 3%	97	3	20	3	76.4	2.4	18.2	3.0
PP/OD/ZL 5%	97	3	20	5	74.9	2.3	17.8	5.0
PP/OD/ZL 10%	97	3	20	10	71.4	2.2	17.0	9.4
PP/OD/ZL 20%	97	3	20	20	65.2	2.0	15.5	17.3
PP/OD/ZL 30%	97	3	20	30	59.9	1.9	14.3	23.9

*Fusabond® E588 as a compatibilizer.

electron microscope (FEI Co. Ltd., Hillsboro, Oregon, USA). Before examination, all the samples were coated with thin Pt/Pd layers. To investigate the morphology of the composite films, wide-angle X-ray diffraction (WAXD) patterns were obtained using a D/MAX-2500 high-/low-temperature X-ray diffractometer (Rigaku Co. Ltd., Tokyo, Japan) equipped with a Cu-K α radiation source. The WAXD data were used to estimate the mean intermolecular distance (d -spacing), crystallinity, and crystal sizes. The d -spacings of the PP/OD/ZL composite films were calculated using Equation (1):

$$n \cdot \lambda = 2d \cdot \sin \theta \quad (1)$$

where n is the reflection order, λ ($= 1.5406 \text{ \AA}$) is the wavelength of the Cu-K α X-ray radiation, d is the mean intermolecular distance, and θ is the diffraction angle [2, 19, 20]. Subsequently, the percent crystallinity ($X_{c, \text{WAXD}}$) was evaluated from the WAXD data according to Equation (2):

$$X_{c, \text{WAXD}} = \frac{\sum A_{\text{crist}}}{\sum A_{\text{crist}} + \sum A_{\text{amorp}}} \quad (2)$$

where A_{crist} and A_{amorp} are the integral areas of the crystalline and amorphous peaks for the composite films, respectively [2].

The densities of the composite films were measured using an AccuPyc II 1340 pycnometer (Micromeritics Instrument Co., Norcross, USA).

3.2. Chemical structure

To analyze the chemical and/or physical interactions between PP, OD, and ZL species in the composite films, Fourier transform infrared (FTIR) spectra were recorded using a Spectrum 65 spectrometer (Perkin-Elmer Co. Ltd., Waltham, Massachusetts, USA) in the range of 400 to 4000 cm^{-1} in the attenuated total reflection mode.

3.3. Thermal properties

To determine the thermal stability of the ZL and PP/OD/ZL composite films, thermogravimetric analysis (TGA) was performed on a 4000 TGA analyzer (PerkinElmer Co. Ltd., Waltham, Massachusetts, USA) at a heating rate of 10 °C/min from 50 to 700 °C under N_2 atmosphere. Furthermore, differential scanning calorimetry (DSC) was conducted using a Q10 calorimeter (TA Instruments Co. Ltd., New Castle Delaware, USA) under N_2 atmosphere. The samples

were heated from –40 to 200 °C at a rate of 10 °C/min. Percent crystallinity ($X_{c, \text{DSC}}$) were calculated from the DSC data using Equation (3):

$$X_{c, \text{DSC}} = \frac{\Delta H_{\text{m}}}{\Delta H_{\text{m}}^0} \cdot 100 \quad (3)$$

where ΔH_{m} is the melting enthalpy of the composite film, and ΔH_{m}^0 is the melting enthalpy of a fully crystalline PP sample (209 J/g) [11, 21].

3.4. Oxygen and water vapor permeabilities

OTRs for the PP/OD/ZL composite films were measured with an OTR 8001 O_2 permeability tester (Systech Instruments Co. Ltd., Johnsburg, Illinois, USA), while the corresponding WVTR values were evaluated by using a WVTR 8002 water vapor permeability tester (Systech Instruments Co. Ltd., Johnsburg, Illinois, USA). To investigate the effect of temperature on the obtained material permeability values, the OTR and WVTR tests were performed at 10, 15, 23, 26.5, 38, and 48 °C.

3.5. Contact angle and surface properties

Contact angle and surface properties of the PP/OD/ZL composite films were investigated using a Phoenix 300 contact angle goniometer (SEO Co. Ltd., Suwon, Korea), while their surface free energies (γ^s) were measured via the Owens–Wendt geometric mean equation, which utilized the theory of adhesion between films and solvents [2, 19, 22]. Polar water ($\gamma^s = 72.8 \text{ mJ/m}^2$, $\gamma^p = 51.0 \text{ mJ/m}^2$, $\gamma^d = 21.8 \text{ mJ/m}^2$) and nonpolar diiodomethane ($\gamma^s = 50.8 \text{ mJ/m}^2$, $\gamma^p = 50.4 \text{ mJ/m}^2$, $\gamma^d = 0.4 \text{ mJ/m}^2$) were employed during measurements [2, 19, 22]. Furthermore, the solubility parameter δ , which serves as an indicator of the hydrophilicity or hydrophobicity of a polymer surface, was calculated by using Equation (4) [2, 19, 23, 24]:

$$\delta = (e_{\text{coh}})^{1/2} \quad (4)$$

where e_{coh} is the cohesive energy density of the PP/OD/ZL composite films calculated using Equation (5) [2, 19, 23, 24]:

$$\gamma^s = 0.75 \cdot (e_{\text{coh}})^{2/3} \quad (5)$$

3.6. Mechanical properties

Mechanical properties of the PP/OD/ZL composite films were measured using a universal testing

machine, QM 100T, equipped with a MC tester version 12.6.0 for analysis (Qmesys Co. Ltd., Kwangmyeong, Korea) according to ASTM D 638–14 (ASTM 2014) and D882–12 (ASTM 2012) specifications. The measurements were performed at a test speed of 500 mm/min and cell load of 5 kg for specimens with 1 cm width and 8 cm length.

3.7. Physical properties of the composite films exposed to food simulants and thermal treatment

When the food application of the as-prepared composite films, it is considered contacts with water-based, alcohol-based, acid-based, and lipid-based products [15, 16]. Therefore, food contact simulations were performed in accordance with Regulation (EC) No 1935/2004 [17] and Regulation (EU) No 10/2011 [18] by using four different substances (distilled water at 40 °C for 10 day, 3% v/v acetic acid at 40 °C for 10 day, 10% v/v ethanol at 40 °C for 10 day, and iso-octane at 20 °C for 2 day) [16–18]. 300 mL of a simulant was placed inside a 500 mL tray containing five film specimens with sizes of 12 cm×15 cm and subsequently covered. After the time of contact with the food simulants has passed, the specimens were removed from the tray, washed with distilled water, and dried inside an oven at 30 °C for 2 day. Before the analysis, the composite films were stored at room temperature for 1 day, after which the effect of food simulants on their O₂ permeability and mechanical properties was investigated.

In order to identify reproducibility of physical properties in the PP/OD/ZL composite films after exposed thermal treatment, the composite films were placed inside the drying oven at 50 °C for 2 day and then transferred into a refrigerator with a temperature of 5 °C for 2 day. After the thermal treatment, the effect on the O₂ permeability and mechanical properties of the PP/OD/ZL composite films were analyzed.

4. Results and discussion

4.1. Preparation of the PP/OD/ZL composite films

The chemical structures of PP, OD, and ZL in the as-prepared composite films as well as their interfacial interactions were analyzed by FTIR spectroscopy. As shown in Figure 2, ZL exhibits several characteristic peaks [25, 26]: asymmetric stretching vibrations of the external linkages between TO_4 tetrahedra ($\text{T} = \text{Si}$ or Al) at 1226 cm^{-1} , asymmetric and symmetric

stretching vibrations of T–O–T at 1066 and 800 cm^{-1} , respectively, vibrations at 544 cm^{-1} assigned to a pentasil structure consisting of five membered rings and T–O bending vibrations of the SiO_4 and AlO_4 internal tetrahedra at 428 cm^{-1} . In these rings, the vertices contained either Si or Al atoms linked through O atoms. The stretching vibration peaks of C=O in Fusabond® E588 could be observed at 1712 cm^{-1} [27]. The obtained PP/OD/ZL composites exhibited characteristic peaks at the same positions as those observed for the PP/OD composite film without ZL [11, 28–30]: The $-\text{CH}_3$ asymmetric stretching vibrations at 2950 cm^{-1} , symmetric stretching vibrations of $-\text{CH}_2-$ at 2838 and 2918 cm^{-1} , that of $-\text{CH}_3$ at 2868 cm^{-1} , $-\text{CH}_3$ asymmetric deformation vibrations at 1454 cm^{-1} and $-\text{CH}_3$ symmetric deformation vibrations at 1376 cm^{-1} , carbon lattice pulsations at 1302 and 1256 cm^{-1} , wagging and deformation vibrations of $-\text{CH}_3$ and $-\text{CH}_2-$ at 1166 cm^{-1} , rocking vibrations of $-\text{CH}_3$ at 998 and 974 cm^{-1} and those of $-\text{CH}_2-$ at 842 and 808 cm^{-1} , and in-plane rocking vibrations of $-\text{CH}_3$ at 717 cm^{-1} originating from the presence of OD species. Further, the characteristic peaks of ZL gradually increased with an increase in the ZL content of the composite films; the peaks shifted from 1066 to 1102 cm^{-1} and 800 to 810 cm^{-1} for T–O–T, from 544 to 538 cm^{-1} for the pentasil structure, and from 428 to 440 cm^{-1} for TO. In addition, the shift of carbonyl group (C=O) stretching of the maleic anhydride from 1712 to 1646 cm^{-1} could be observed, which might be related with physical interaction between Fusabond® E588, ZL, OD and PP.

Figure 2. FTIR spectra of ZL, OD, and the PP/OD/ZL composite films.

These shifts in the characteristic peaks indicate some changes in the chemical interaction between the three species in the composite films. As hydrophobic ZLs contain high amounts of $\text{SiO}_2/\text{Al}_2\text{O}_3$, van der Waals or dipole-dipole interactions are usually involved in the adsorption process [14], which may strengthen the interfacial interaction between the OD or PP and ZL species in the composite films. These interactions may lead to improvements in the thermal stability and mechanical properties of the films.

4.2. Morphology of the PP/OD/ZL composite films

Analyzing the morphology of the organic/inorganic composites is valuable for assessing their thermal, mechanical, and gas permeation properties [2, 3, 5, 8, 31]. Figure 3 shows the WAXD patterns of ZL and the PP/OD/ZL composite films, and the associated numerical values are summarized in Table 2. The XRD pattern of ZL shows several sharp diffraction peaks at $2\theta = 7.9, 8.7, 14.7, 23.0, 23.9$ and 24.5° ,

which correspond to (011), (020), (031), (051), (303) and (313) planes of the ZSM-5 zeolite structure [14, 32, 33].

In contrast, the PP/OD composite film without ZL yielded an amorphous halo in the 2θ range of $15\text{--}25^\circ$ as well as four sharp diffraction peaks at $2\theta = 14.0, 16.9, 18.5$, and 21.5° , which are attributed to the (110), (040), (130), and (301) crystal planes of pure PP, respectively [34]. Furthermore, the XRD patterns of the five PP/OD/ZL composite films with 3–30 wt% ZL show several crystalline peaks that are almost identical to those observed for pure ZL in the 2θ range of $5\text{--}30^\circ$, with their intensities proportional to the ZL content [14, 32]. As the ZL content increased from 0 to 30%, the mean intermolecular distance related to the 2θ values of the (110), (040), (130), and (200) crystal planes of PP in the composite films slightly decreased in accordance with Bragg's law (see Table 2). The obtained WAXD results indicate that the incorporation of ZL slightly enhances the molecular ordering in the crystalline structure of the

Table 2. WAXD and density values for the PP/OD/ZL composite films.

Sample code	WAXD								Density	
	(110)		(040)		(130)		(301)		$X_{\text{c, WAXD}}$	$[\text{g}/\text{cm}^3]$
	2θ [$^\circ$]	d -spacing [$\text{\AA}$]	2θ [$^\circ$]	d -spacing [$\text{\AA}$]	2θ [$^\circ$]	d -spacing [$\text{\AA}$]	2θ [$^\circ$]	d -spacing [$\text{\AA}$]		
PP/OD/ZL 0%	14.01	6.32	16.82	5.27	18.44	4.81	21.58	4.12	31.8	0.92
PP/OD/ZL 3%	13.98	6.33	16.86	5.26	18.46	4.80	21.83	4.07	32.3	0.93
PP/OD/ZL 5%	14.02	6.31	16.90	5.24	18.51	4.79	21.70	4.09	33.7	0.93
PP/OD/ZL 10%	14.01	6.32	16.86	5.26	18.49	4.80	21.81	4.07	34.3	0.95
PP/OD/ZL 20%	14.04	6.31	16.91	5.24	18.49	4.80	21.79	4.08	35.1	0.96
PP/OD/ZL 30%	14.05	6.30	16.92	5.24	18.52	4.79	21.98	4.04	37.8	1.00

Figure 3. WAXD patterns for (a) ZL and (b) the PP/OD/ZL composite films.

PP/OD/ZL composite film. Therefore, the percent crystallinity values for the five PP/OD/ZL composite films are higher than that for the PP/OD composite film without ZL.

The density of the composite films increased from 0.92 to 1.00 g/cm³ with an increase in the ZL content, which might be possibly due to the enhanced interfacial interactions between PP and OD, as observed

by FTIR measurements (see Figure 2 and Table 2). Although PP and OD have similar non-polar chemical structures, their interfacial interaction is not strong enough to yield a good dispersion, owing to the highly mismatched flowability related to different molecular weights [31]. An increase in the content of hydrophobic ZL with the porous non-polar structure was expected to decrease the flowability of the

Figure 4. SEM images of the fractured surface in PP/OD/ZL composite films.

low molecular weight OD, matching the flowability of OD with that of PP and finally leading to a good dispersion of OD in PP.

To determine the dispersion state and interfacial interaction of the ZL particles in the PP/OD/ZL composite films, SEM analyses of the fractured surfaces of the PP/OD/ZL composite films were performed (Figure 4). Our previous study showed that the adhesion and interfacial interaction between non-polar OD and non-polar PP was maintained to some degree at a high OD content in the PP matrix [8]. Likewise, there were no cracks or voids on the fractured surface of the PP/OD composite film without ZL. As ZL with a relatively high Si/Al ratio has a hydrophobic chemical structure, it may interact well with PP and OD [14]. Thus, this will prevent the production of defects such as inner cracks and voids originating from weak interfacial interaction between the different components of the composite films. In this study, ZL was observed to be well-embedded in PP/OD matrix as ascertained by SEM analyses of the fractured composite films. This indicates that ZL strongly interacts with PP and OD [35]. However, agglomeration of ZL in the PP/OD matrix increased slightly with an increase in the ZL content. In our previous study, the different flowabilities of PP and OD originating from the difference in their molecular weights could have increased the phase separation of PP and OD, thereby significantly affecting the physical properties of the PP/OD/ZL composite films [8]. However, after the introduction of ZL into the PP/OD matrix, no discernible phase separation was observed. According to the FTIR, SEM, WAXD, and density measurement results, the interfacial interaction and crystallinity of the composite films were enhanced upon adding ZL. This might be because ZL aided in controlling the flowability of OD with respect to the PP phase.

4.3. Thermal properties

For many packaging applications, the polymeric material is required to possess high thermal stability to endure high-temperature treatments such as extrusion and injection molding, as well as the sterilization process [36, 37], while a strong interfacial interaction between the polymer and the additives may significantly affect the thermal properties [37]. As shown in Figure 5 and Table 3, all the composite films exhibit two-step degradation processes similar to those observed for PP/OD composite films without ZL, indicating that the ZL content did not significantly

influence the thermal degradation characteristic of the composite films. In addition, the residual ZL content measured at 700 °C is consistent with the corresponding theoretical ZL content, demonstrating that the ZL particles were successfully incorporated into the PP/OD matrix. The first degradation stage between 130 and 340 °C is due to the decomposition of OD near its flash temperature [38, 39] or evaporation before the boiling temperature of OD [39, 40] while the second degradation stage between 340 and 480 °C results from the bond scission and chain transfer reactions of the PP trimers in pure PP [41, 42]. With increasing ZL content from 0 to 30%, the decomposition temperature increased from 170.2 to 187.6 °C for a 1 wt% decomposition ($T_{d1\%}$) and from 308.5 to 399.9 °C for a 10 wt% decomposition ($T_{d10\%}$), respectively. Such enhancement of the thermal stability of the PP/OD/ZL composite films can be attributed to the structural changes originating from the interfacial interaction between the PP, OD, and ZL species. Based on the shift of the characteristic peaks of ZL identified by FTIR analysis, decrease of intermolecular mean distance of the crystal planes of PP calculated by Bragg's law, and good adhesion between ZL and PP/OD matrix observed by SEM analysis, presumably, the non-polar porous ZL particles strongly interact with the non-polar OD and PP species. These interfacial interactions and the ZL porous structure may restrict the chain mobility and thus enhance the thermal stability of the obtained composite films.

Phase transitions from the crystalline to amorphous structures produce significant changes in the physical

Figure 5. TGA curves of the PP/OD/ZL composite films.

Table 3. Thermal properties of the PP/OD/ZL composite films.

Sample code	DSC										TGA			
	T_{m1}^a [°C]	T_{m2}^a [°C]	ΔH_{m1}^b [J/g]	ΔH_{m2}^b [J/g]	ΔH_{total}^c [J/g]	T_{c1}^d [°C]	T_{c2}^d [°C]	ΔH_{c1}^e [J/g]	ΔH_{c2}^e [J/g]	X_c^f	$T_{d1\%}^g$ [°C]	$T_{d3\%}^g$ [°C]	$T_{d10\%}^g$ [°C]	[wt%] ^h
PP/OD/ZL 0%	21.8	161.4	15.5	84.3	99.8	2.7	107.9	14.6	86.9	47.8	170.2	204.9	308.5	0.7
PP/OD/ZL 3%	18.0	159.1	15.2	90.5	105.7	4.0	110.1	12.7	90.1	49.2	172.8	207.1	314.3	2.5
PP/OD/ZL 5%	19.0	160.4	11.4	89.0	100.4	4.8	113.2	10.7	88.6	48.0	174.8	214.6	341.2	4.0
PP/OD/ZL 10%	17.9	160.9	10.0	88.8	98.8	3.0	117.6	9.2	88.9	47.3	176.4	212.2	357.3	5.9
PP/OD/ZL 20%	12.1	162.4	5.3	87.6	92.9	−4.6	120.8	4.0	87.1	44.4	185.3	228.8	380.7	12.8
PP/OD/ZL 30%	9.1	162.6	2.8	79.8	82.6	−7.4	119.1	2.8	79.0	39.5	187.6	232.8	399.0	16.4

^aMelting temperature of PP/OD/ZL composite films.^bMelting enthalpy of of PP/OD/ZL composite films.^cTotal melting enthalpy of PP/OD/ZL composite films.^dCrystallization temperature of PP/OD/ZL composite films.^eCrystallization enthalpy of PP/OD/ZL composite films.^fCrystallinity of PP/OD/ZL composite films by DSC analysis.^g1, 3, and 10% decomposition temperature of PP/OD/ZL composite films.^hWeight residue in PP/OD/ZL composite films at 700 °C.

properties of the polymeric materials, such as O₂ and water vapor permeabilities [1–3, 5–8]. To investigate possible phase transitions in the composite films, DSC analysis was conducted (Figure 6 and Table 3). The PP/OD composite film without ZL exhibited two endothermic peaks at 21.8 and 161.4 °C during heating and two exothermic peaks at 2.7 and 107.9 °C during cooling. The melting enthalpy (ΔH_m) and crystallization enthalpy (ΔH_c) of the PP/OD composite film without ZL are 15.5 and 84.3 J/g for heating and 14.6 and 86.9 J/g for cooling, respectively. The first peak is associated with the phase transition in the OD species, while the second peak is related to the phase transition originating from the PP melting [11, 21].

Figure 6. DSC curves of the PP/OD/ZL composite films.

The initial melting (T_{m1}) and crystallization (T_{c1}) temperatures of the OD phases for the composite films decreased from 21.8 to 9.1 °C and 2.7 to −7.4 °C, respectively, whereas the ΔH_{m1} and ΔH_{c1} values of the OD crystalline phases (corresponding to the melting and crystallization temperatures, T_{m1} and T_{c1} , respectively) decreased from 15.5 to 2.8 J/g and from 14.6 to 2.8 J/g, respectively, with an increase in the ZL content from 0 to 30%. As the ZL content increases, the OD fraction in the PP matrix decreases, resulting in a broad small DSC feature corresponding to the OD crystalline structure in the composite films. This indicates that decreased OD contents in the PP matrix produce fewer changes in the morphological structure of the composite films due to variations in the ZL content.

The presence and relative amount of ZL strongly affect the melting and crystallization behaviors of the PP phases in the composite films. Thus, the second melting (T_{m2}) and crystallization (T_{c2}) temperatures increased from 161.4 to 162.6 °C and from 107.9 to 119.1 °C, respectively, with an increase in the ZL content from 0 to 30%, while the corresponding ΔH_{m2} and ΔH_{c2} values for the PP crystalline phases increased only slightly, indicating that ZL acts as a nucleating agent for the PP crystalline phases in the PP/OD/ZL composite films. However, the PP crystalline fractions of the PP/OD/ZL composite films significantly decreased with an increase in the ZL content to 30% because high ZL contents inhibit the formation of a PP crystalline phase [11].

The total ΔH_m and ΔH_c values for the PP/OD/ZL composite films slightly increased with an increase

in the ZL content up to 5% and then significantly decreased. The obtained results are inconsistent with the WAXD data described earlier and may be explained by the complexity of PP, OD, and ZL compositions in the composite films. First, the fraction of the ZL crystalline structure in the composite films increases upon the introduction of ZL; however, it could not be identified by the DSC analysis due to the unchanged ZL morphology during melting or crystallization. In addition, the crystalline structures corresponding to the OD and PP phases in the composite films were differently affected by the increase in the ZL content. Overall, the presence of OD alters the morphological structure of the PP matrix. This can possibly change their morphologies depending on the phase change temperature originating from the OD addition. After introducing ZL with the non-polar and porous structure into the composite films, however, ZL strongly interacts with the low molecular weight OD and thus restricts its chain mobility. As a result, the temperature-dependent morphological changes in the composite films originating from the OD addition become less intense upon the addition of ZL.

4.4. Oxygen and water vapor permeability

Figure 7 shows the oxygen and water vapor permeability values for the PP/OD/ZL composite films with corresponding DSC analysis. In our previous study, the magnitudes of oxygen and water vapor permeation jumps started to increase between 10 and 30 °C depending on the OD content in PP [8]. The OTR and WVTR for the PP/OD composite film with 0% ZL increased from 7739 to 34235 cc/m²·day and from 3.1 to 33.1 g/m²·day, respectively, with an increase in

temperature from 10 to 48 °C. However, OTR and WVTR values of PP/OD/ZL 0% composite films were different from them of PP/OD 20% composite films [8]. This may due to be modified the surface properties in the PP/OD 20% matrix by adding the Fusabond® E588 with amphiphilic property.

The OTRs for the PP/OD/ZL composite films also increased from 7056 to 31 945 cc/m²·day, from 6306 to 28 524 cc/m²·day, from 5104 to 22 518 cc/m²·day, from 3749 to 20 376 cc/m²·day, and from 2293 to 16 204 cc/m²·day. The trends of obtained WVTR data for the PP/OD/ZL composite films were similar to the OTR ones, increasing from 1.7 to 29.4 g/m²·day, from 1.6 to 29.1 g/m²·day, from 1.5 to 28.8 g/m²·day, from 1.3 to 27.8 g/m²·day, and from 1.0 to 25.6 g/m²·day with a temperature increase from 10 to 48 °C. Although the OTRs and WVTRs for the composite films increased with increasing temperature, the permeation jumps decreased at higher ZL contents. To identify the O₂ and water vapor permeation behavior of PP/OD/ZL composite films as a function of temperature, we used the Arrhenius equation, as described by Equation (6):

$$\ln P = \ln P_0 - \frac{E_a}{RT} \quad (6)$$

where P (O₂ and water vapor: mols·m/m²·s·Pa) is the permeability of the composite film, P_0 represents the permeability coefficient of composite films, E_a [J/mol] is the activation energy for penetrants, R [J/(mol·K)] is an universal gas constant, and T [K] explains absolute temperature [3, 28, 43].

We chose the reference temperature, 26.5 °C, to compare intermediate state and completely melting state

Figure 7. (a) OTR and (b) WVTR curves for the PP/OD/ZL composite films.

Table 4. Comparison of oxygen (OP) and water vapor permeation (WVP) coefficient and activation energy of PP/OD/ZL composite films.

Sample code	Temperature range [°C]													
	OP							WVP						
	10~23 °C			30~48 °C			$\frac{E_{op+26.5}}{E_{op-26.5}}$	10~23 °C			30~48 °C			$\frac{E_{wv+26.5}}{E_{wv-26.5}}$
	$P_{op-26.5}$	$E_{op-26.5}$	R^2	$P_{op+26.5}$	$E_{op+26.5}$	R^2		$P_{wvp-26.5}$	$E_{wvp-26.5}$	R^2	$P_{wvp+26.5}$	$E_{wvp+26.5}$	R^2	
PP/OD/ZL 0%	-18.0	36,615	1.00	-27.3	12,673	0.87	0.34	-18.7	63,527	0.99	-30.2	35,126	0.97	0.55
PP/OD/ZL 3%	-19.0	34.553	0.99	-25.9	16.769	0.91	0.49	-16.4	70.427	0.99	-26.0	46.782	0.99	0.66
PP/OD/ZL 5%	-20.9	30.446	0.99	-22.5	25.947	0.96	0.85	-17.4	68.357	0.99	-23.0	54.930	0.99	0.80
PP/OD/ZL 10%	-18.4	36.690	0.99	-25.6	18.531	0.98	0.58	-21.3	59.270	0.99	-21.2	59.669	0.99	1.00
PP/OD/ZL 20%	-16.2	42.618	0.99	-24.6	21.360	0.99	0.50	-19.3	64.267	0.99	-21.0	60.426	0.99	0.94
PP/OD/ZL 30%	-18.5	38.394	0.98	-22.1	28.783	0.98	0.75	-22.1	58.339	0.99	-15.7	74.734	0.99	1.28

of OD portion in PP matrix. As the melting point of OD in PP matrix is traversed, the intensity of changes in activation energies for O₂ and water vapor permeation of PP/OD/ZL 0% composite film was significantly decreased depending on the temperature (Table 4). As increase of ZL content in PP matrix, it is apparently showed that the magnitude of decrease in activation energy for O₂ and water vapor permeation is relatively weak depending on the temperature change (Table 4). This is due to be hindered temperature-dependent morphological changes of OD resulting from the incorporation of ZL in PP matrix. That is, the incorporation of ZL prevents various penetrants such oxygen and water molecules from being absorbed and diffused into the PP/OD matrix. From these results, the observed decrease in the temperature-dependence of the oxygen and water vapor permeation jumps for the PP/OD/ZL composite films may be due to the change in their chemical and morphological structures originating from the ZL addition.

To further study effect on morphological changes against the oxygen and water vapor permeability, we have used a modified two-phase model proposed by Michaels and Bixler [28], and others [3, 5, 8] which takes into account both crystalline and amorphous structures as described by Equation (7):

$$P_c = P_a \cdot \frac{1 - \Phi}{\tau \beta} \quad (7)$$

where P_c is the permeability of the composite film with both the amorphous and crystalline structures, P_a represents the permeability of the amorphous structure in the composite films, Φ is the volume fraction of the PP and ZL crystalline structures, τ is the tortuosity factor originating from the presence of PP and

ZL, and β is the factor related to the immobilization of amorphous structure owing to the PP and ZL crystalline structures. As shown in Figure 6, OD exhibits a phase-switchable morphological structure in the composite films in the temperature range between 10 and 30 °C. When the temperature increased from 10 to 30 °C, the crystalline structure of OD started to change into the amorphous one, leading to an increase in the chain mobility of OD in the PP matrix. As a result, the OD species in the composite films acted as temperature-dependent permeation channels for oxygen and water vapor molecules. However, the permeation jump was reduced with an increase in the ZL content because both the PP crystalline and porous nonpolar ZL phases might inhibit the temperature-dependent morphological conversion from the OD crystalline structure to the amorphous one.

The increase in the volume fraction of the ZL crystalline phase enhanced the related OD/ZL and PP/ZL interfacial interactions, which constantly maintained the immobilization of the OD species in the composite films during the OD phase change with increasing temperature. Note that the PP and ZL crystalline regions in the films are considered impermeable to oxygen and water vapors due to the formation of tortuous channels that prevent penetrants from sorption and diffusion into the composite films [19, 20]. As a result, the permeation jumps for oxygen and water vapors decreases.

4.5. Contact angle and surface properties

To investigate further variations in the surface properties of the PP/OD/ZL composite films due to variable ZL contents, their contact angles and surface energies were measured at 23 °C. As shown in Table 5,

Table 5. Contact angles, surface energies, cohesive energy densities, and solubility parameters for the PP/OD/ZL composite films.

Sample code	Contact angle [°]		Surface energy, γ^s [mJ/m ²]			$e_{\text{coh}} \cdot 10^6$ [J/m ³]	$\delta \cdot 10^3$ [J ^{1/2} /m ^{3/2}]
	Water	Diiodomethane	Total	Dispersive	Polar		
PP/OD/ZL 0%	84.1	35.6	42.2	40.2	2.0	422.1	20.5
PP/OD/ZL 3%	87.4	41.5	39.1	37.5	1.6	376.4	19.4
PP/OD/ZL 5%	88.6	43.2	38.1	36.7	1.4	362.1	19.0
PP/OD/ZL 10%	89.4	43.9	37.7	36.4	1.3	356.4	18.9
PP/OD/ZL 20%	92.6	45.7	36.5	35.7	0.8	339.5	18.4
PP/OD/ZL 30%	94.6	48.1	35.1	34.5	0.6	320.2	17.9

the PP/OD/ZL 0% composite film without ZL content was characterized by a water contact angle of 84.1° and diiodomethane contact angle of 35.6°. This results are different from result of water contact angle (101.2°) and diiodomethane contact angle of PP/OD 20% (43.4°) composite films, as described in our previous study [8]. By adding the Fusabond® E588 with amphiphilic properties, affinity against both water molecules and lipid materials of PP/OD/ZL 0% composite films were slightly increased. In terms of the chemical structure of composite films, water vapor permeability of composite films strongly has been changed as an increase of hydrophilicity [8, 44]. This coincides with the water vapor permeability results of PP/OD/ZL composite films, as shown in Figure 7. Increasing the ZL content in the PP/OD/ZL composite films increased the corresponding water contact angles from 84.1 to 94.6° and diiodomethane contact angles from 35.6 to 48.1°. The obtained results indicate that the hydrophobicity of the PP/OD/ZL composite films increased only slightly, while the potential interaction of the nonpolar liquid with the PP/OD/ZL composite films decreased with an increase in the ZL content.

The total surface free energy contains polar and dispersive surface components, which are equal to 2.0 and 40.2 mJ/m² for the PP/OD composite film with 0% ZL. However, increasing ZL content decreases the polar energy of the PP/OD/ZL composite films from 2.0 to 0.6 mJ/m² and the corresponding dispersive energy from 40.2 to 34.5 mJ/m². Overall, increasing ZL content decreases the total surface free energy from 42.2 to 35.1 mJ/m². The observed trends for the composite surface energy are similar to those obtained for the solubility parameter, which was equal to $20.5 \cdot 10^3 \text{ J}^{1/2}/\text{m}^{3/2}$ for PP/OD with 0% ZL and slightly decreased to $17.9 \cdot 10^3 \text{ J}^{1/2}/\text{m}^{3/2}$ for the PP/OD/ZL composite films, while the solubility parameter of water was $47.9 \cdot 10^3 \text{ J}^{1/2}/\text{m}^{3/2}$ [2, 8, 23]. Thus, the

difference between the solubility parameters for the composite films and water vapors was slightly increased by adding hydrophobic and non-polar ZL species, indicating that it was difficult for water vapors to penetrate into the PP/OD/ZL composite films.

4.6. Mechanical properties

The mechanical properties of pure PP and three different PP/OD/ZL composite films were investigated using the universal testing machine, and the obtained results are summarized in Figure 8 and Table 6 [13, 45, 46]. The tensile strength and elongation at break of pure PP are 39.0 MPa and 255.4%, respectively. The tensile strength and elongation at break of the PP/OD composite film without ZL are lowered to 23.1 MPa and 219.6%, respectively. This might be due to the low interfacial interaction between PP and OD and poor dispersion and agglomeration originating from OD-OD interaction. In addition, the OD addition might prevent the formation of a PP continuous phase, causing the initiation and propagation of stress cracking during the film deformation [13].

Figure 8. Tensile strength and elongation at break of the PP/OD/ZL composite films.

Table 6. Tensile strength and elongation at break results for the PP/OD/ZL composite films after the contact with the food simulants and thermal treatment.

Tensile strength [MPa]						
Sample code	Standard	DI water (10 days at 40 °C)	3% acetic acid (10 days at 40 °C)	10% ethanol (10 days at 40 °C)	isooctane (10 days at 40 °C)	50 °C (2 days) → 5 °C (2 days)
PP/OD/ZL 0%	23.1±0.6	23.2±0.6 (100.4)	22.6±1.1 (97.9) ^a	22.9±1.8 (99.3) ^a	21.8±0.9 (94.3) ^a	23.6±2.0 (101.9)
PP/OD/ZL 3%	33.1±0.8	31.1±1.1 (94.1) ^a	33.2±1.0 (100.3) ^a	32.4±2.0 (98.0) ^a	25.9±1.0 (78.5) ^a	30.7±1.5 (93.0) ^a
PP/OD/ZL 5%	32.0±0.4	29.2±1.0 (91.2) ^a	29.4±2.0 (91.8) ^a	30.1±2.2 (94.1) ^a	25.0±0.6 (78.6) ^a	30±1.6 (96.6) ^a
PP/OD/ZL 10%	29.9±0.7	27.4±2.0 (91.4) ^a	26.4±0.4 (88.0) ^a	28.7±0.7 (95.8) ^a	26.3±0.9 (87.7) ^a	29.2±1.6 (97.3) ^a
PP/OD/ZL 20%	29.0±0.9	27.2±1.3 (93.9) ^a	27.6±1.4 (95.4) ^a	28.0±1.1 (96.7) ^a	27.6±1.3 (95.3) ^a	28.9±1.8 (99.7) ^a
PP/OD/ZL 30%	31.5±0.8	27.9±1.7 (88.5) ^a	30.7±1.6 (97.2) ^a	27.9±2.6 (88.6) ^a	27.4±1.5 (86.8) ^a	29.7±2.0 (94.8) ^a
Elongation at break [%]						
Sample code	Standard	DI water (10 days at 40 °C)	3% acetic acid (10 days at 40 °C)	10% ethanol (10 days at 40 °C)	isooctane (10 days at 40 °C)	50 °C (2 days) → 5 °C (2 days)
PP/OD/ZL 0%	219.6±6.1	217.5±13.0 (99.1) ^b	206.5±12.8 (94.0) ^b	212.4±5.1 (96.7) ^b	6.0±0.4 (2.7) ^b	224.7±7.7 (102.3) ^b
PP/OD/ZL 3%	358.8±12.2	338.5±14.5 (94.3) ^b	335.0±6.8 (93.4) ^b	335.6±14.7 (93.5) ^b	255.7±10.0 (71.3) ^b	323.2±13.9 (90.1) ^b
PP/OD/ZL 5%	355.5±15.8	300.0±10.5 (84.4) ^b	309.3±21.8 (87.0) ^b	345.3±13.4 (97.1) ^b	335.0±12.1 (66.1) ^b	338.0±16.2 (95.1) ^b
PP/OD/ZL 10%	302.1±7.2	280.4±10.9 (92.8) ^b	261.9±17.7 (86.7) ^b	274.9±8.5 (91.0) ^b	257.4±13.4 (85.2) ^b	303.9±8.4 (100.6) ^b
PP/OD/ZL 20%	284.7±10.8	264.0±11.5 (92.7) ^b	281.0±11.7 (98.7) ^b	251.4±13.9 (88.3) ^b	279.2±9.1 (98.0) ^b	294.5±14.7 (103.4) ^b
PP/OD/ZL 30%	273.5±9.1	236.7±9.3 (86.5) ^b	250.9±7.9 (91.7) ^b	264.6±15.5 (96.8) ^b	252.6±10.7 (92.3) ^b	261.3±10.8 (95.5) ^b

^aRetention rate [%] of tensile strength in test samples after stressed treatment.^bRetention rate [%] of elongation at break in test samples after stressed treatment.

However, compared to the PP/OD composite film without ZL, the PP/OD/ZL composite films exhibited enhanced tensile strength and elongation at break owing to the ZL non-polar porous structure. The probable reason for this is that ZL with its hydrophobic and non-polar structure physically interacted well with relatively low molecular weight OD, which decreased the flow rate of OD in the composite films during the extrusion process. Furthermore, the porous ZL species might immobilize the OD and PP chains at the PP/OD interface. This can aid in maintaining a constant thickness of the composite films and uniform dispersion of the OD molecules in the PP matrix by modulating the flowability of the two components of different molecular weights. As a result, the tensile strength and elongation at break of the composite films are enhanced.

4.7. Physical properties of the composite films exposed to food simulants and thermal treatment

In order to protect packaging applications from contamination, it is critical to evaluate physical properties of a packaging material after the contact with various products, high pressure, or thermal treatment [15, 16]. In this study, we have investigated the OTRs and mechanical properties of the composite films exposed to four different food simulants and thermal treatment. The effects of the food simulants and thermal treatment on the mechanical properties of the PP/OD/ZL composite films are presented in Table 6. The stress treatment performed using deionized water, acetic acid, and ethanol as well as heat treatment produced slight deteriorations of mechanical properties of the composite films with variations not exceeding

Table 7. OTR data obtained for the PP/OD/ZL composite films after the contact with food simulants.

Sample code	OTR [cc/m ² ·day at 23 °C]				
	Standard	DI water (10 days at 40 °C)	3% acetic acid (10 days at 40 °C)	10% ethanol (10 days at 40 °C)	isooctane (10 days at 40 °C)
PP/OD/ZL 0%	15 301±161	67 724±2 895 (442.6)*	43 782±3 422 (286.1)*	62 909±2 287 (411.1)*	33 337±900 (217.9)*
PP/OD/ZL 3%	13 486±472	12 577±1 680 (93.3)*	12 852±896 (95.3)*	12 058±1 376 (89.4)*	1 857±91 (13.8)*
PP/OD/ZL 5%	10 871±259	10 658±1 006 (98.0)*	10 310±146 (94.8)*	10 446±310 (96.1)*	1 827±96 (16.8)*
PP/OD/ZL 10%	9 999±379	9 291±616 (92.9)*	9 324±1278 (93.2)*	9 084±369 (90.8)*	1 813±89 (18.1)*
PP/OD/ZL 20%	8 255±334	6 426±800 (77.8)*	6 942±741 (84.1)*	6 680±143 (80.9)*	1 845±111 (22.4)*
PP/OD/ZL 30%	4 627±448	4 897±84 (105.8)*	4 200±22 (90.8)*	4 883±50 (105.5)*	1 631±72 (35.2)*

*Retention rate (%) of OTR in test samples after stressed treatment.

15%. When the PP/OD composite film was exposed to iso-octane, a 97% decrease in elongation at break was observed, which could be attributed to the fact the non-polar chemical structure of iso-octane (which was similar to that of OD) could easily adhere and penetrate into the OD phase or the interface between the OD and PP species, resulting in disruption and decrease in flexibility of the composite morphological structure. However, the elongation at break for the PP/OD/ZL composite films increased with an increase in the ZL content. As indicated by the obtained WAXD, density, and mechanical property data, the incorporation of ZL into the structures of the PP/OD composite films produced enhanced interfacial interactions between PP and OD, which were possibly able to resist contaminations caused by the presence of lipid simulants.

The changes in the OTR values for the PP/OD/ZL composite films produced by the contact with the food

simulants is listed in Table 7. In particular, the OTR value for the PP/OD composite film with 0% ZL was significantly increased after the contact with food simulants since the accompanying morphological changes weaken the interfacial interactions between PP and OD, making it easier for O₂ molecules to penetrate through the composite film surface. However, it can be expected that the addition of ZL into the PP/OD composite film may induce a relatively dense structure containing both the PP and OD species, which would make it difficult for the simulant molecules to dissolve and penetrate into the composite films. As expected, the variations of the OTR values for the PP/OD/ZL composite films did not exceed 25%. However, the observed decrease in the OTR values for the PP/OD/ZL composite films was more prominent in the case of the iso-octane treatment, corresponding to 13.8% for the PP/OD/ZL composite film with 3% ZL. The OD phase of the composite

Table 8. OTR data obtained for the PP/OD/ZL composite films after thermal treatment.

Sample code	OTR [cc/m ² ·day at 23 °C]			
	Standard	1 st cycle	2 nd cycle	3 rd cycle
PP/OD/ZL 0%	15 301±161	14 928±463 (97.6)*	15 208±676 (99.4)*	14 848±469 (97.0)*
PP/OD/ZL 3%	13 486±472	13 737±8 (101.9)*	14 030±681 (104.0)*	13 156±1 028 (97.6)*
PP/OD/ZL 5%	10 871±259	10 497±306 (96.6)*	11 065±139 (101.8)*	11 371±169 (104.6)*
PP/OD/ZL 10%	9 999±379	9 888±292 (98.9)*	10 572±432 (105.7)*	10 284±43 (102.8)*
PP/OD/ZL 20%	8 255±334	7 758±316 (94.3)*	7 915±158 (96.2)*	7 646±100 (92.6)*
PP/OD/ZL 30%	4 627±448	4 794±317 (103.6)*	4 313±373 (93.2)*	4 179±56 (90.3)*

*Retention rate [%] of OTR in test samples after thermal treatment.

films strongly interacted with the iso-octane species, thus removing any obstacles for dissolving and diffusing O₂ molecules into the composite films. The changes in the OTR values for the PP/OD/ZL composite films were measured after thermal treatments at 50 °C for 2 day and 5 °C for 2 day. The experiments were conducted in three cycles. As shown in Table 8, the OTR results obtained after the heat treatment exhibited a trend, which was different from that observed for the OTR data measured after the contact with the food simulants. After the heat treatment, the variations of the OTR values for all the composite films did not exceed 10%. From the practical viewpoint, the PP/OD/ZL composite films are relatively compatible with the heat treatment and thus can be possibly utilized in various fields that require temperature-dependent control of gas permeability properties such as agricultural products for O₂/CO₂ control, medical devices for sterilization, and microwavable products for vapor emission applications.

5. Conclusions

Six different PP/OD/ZL composite films for packaging applications with temperature-dependent permeability properties were prepared. The addition of ZL into PP/OD composite films changed their morphological and chemical structures and increased interfacial interactions between the OD and PP species. The OD phases in the PP/OD/ZL composite films acted as diffusion channels for the temperature-dependent O₂ and water vapor permeation. However, the enhancement of the crystalline structure and interfacial interactions due to the ZL incorporation prevented the movement of the OD species in the composite films near the phase change temperature (between 10 and 30 °C). In addition, the new crystalline regions formed tortuous paths that prevented the sorption and diffusion of O₂ and water vapor molecules into the composite films. As a result, permeation jumps for O₂ and water vapors were reduced near the phase change temperature of OD. However, the incorporation of ZL species with porous and non-polar structures into the PP/OD composites films allows the flowability control between the OD and PP phases originating from their different molecular weights, which improve the dispersion of OD in the PP matrix and interfacial interactions between the PP and OD species. Such an improvement significantly

enhances thermal stability, mechanical properties, and OTRs of the composite films after the contact with food simulants and thermal treatment. As indicated by the obtained results, the PP/OD/ZL composite films can be used as packaging materials to preserve the quality of packaged products by controlling their temperature-dependent gas permeability properties.

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