

Article

Diffusion Coefficients and Activation Energies of Diffusion of Organic Molecules in Poly(lactic acid) Films

Johann Ewender ¹, Rafael Auras ² , Uruchaya Sonchaeng ^{2,3}  and Frank Welle ^{1,*} 

¹ Fraunhofer Institute for Process Engineering and Packaging (IVV), 85354 Freising, Germany; johann.ewender@ivv.fraunhofer.de

² School of Packaging, Michigan State University, East Lansing, MI 48824, USA; aurasraf@msu.edu (R.A.); uruchaya.s@ku.ac.th (U.S.)

³ Department of Packaging and Materials Technology, Faculty of Agro-Industry, Kasetsart University, Bangkok 10900, Thailand

* Correspondence: frank.welle@ivv.fraunhofer.de

Abstract: Poly(lactic acid) (PLA) is one of the most important bio-based and industrial compostable materials in food packaging. Its barrier properties towards oxygen and moisture are well documented. However, data on barrier properties of PLA towards organic molecules are scarce in the literature. This study investigated the diffusion of various organic molecules, including *n*-alkanes, 1-alcohols, 2-ketones, ethers, esters, amines, and aromatics, in two commercial PLA films with thicknesses of 20 μm and 30 μm . The diffusion coefficient (D_P) values were determined from lag time in permeation tests conducted at temperatures ranging from 20 $^{\circ}\text{C}$ to 90 $^{\circ}\text{C}$. The films were also characterized in terms of crystallinity, rigid and mobile amorphous fractions, and molecular weight. Activation energies (E_A) were calculated based on the temperature dependence of the D_P using the Arrhenius approach. In total, 290 D_P values for 55 individual substances were determined, and 38 E_A values were derived from these data. The E_A correlated well with the molecular volume of the investigated substances. Moreover, the pre-exponential factor D_0 showed a correlation with E_A . These correlations enabled the establishment of diffusion modeling parameters for PLA, allowing the prediction of D_P for untested substances. The diffusion behavior of PLA was further compared with the literature data for polyethylene terephthalate and polyethylene naphthalate, providing insights into the relative performance of these materials.

Keywords: barrier testing; activation energy of diffusion; free volume; biodegradable



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1. Introduction

Poly(lactic acid)—PLA—is a leading bio-based and compostable plastic material widely used in food packaging and agricultural applications. Its mechanical, thermal, and structural properties, as well as its barrier performance against oxygen and moisture, have been extensively studied [1,2]. Adequate oxygen and moisture barriers are essential for extending the shelf life of packaged foods. Additionally, the diffusion of organic molecules through PLA determines its effectiveness as a barrier to flavoring substances and influences the migration of substances from PLA packaging into food. However, studies on the barrier properties of PLA towards organic molecules and diffusion coefficients of organic substances in PLA remain scarce because measuring organic vapor diffusion is challenging and requires specialized instrumentation and methodologies [3]. An overview of PLA barrier properties has been published, reporting the lack of these mass transfer data and

the lack of consideration of PLA as a three-phase structure comprising a crystalline fraction, a mobile amorphous fraction, and a rigid (or restricted) amorphous fraction (RAF) [2]. The presence of RAF in semicrystalline PLA plays a crucial role in mass transfer due to the increased free volume, particularly at temperatures below the glass transition temperature, affecting the diffusion of gases and perhaps organic molecules, especially [4].

The migration of polymer ingredients, monomers, additives, and non-intentionally added substances from PLA packaging materials into food or food simulants was also investigated [5–8]. In addition, the sensory properties of PLA are relevant for the food law compliance evaluation of packed products in PLA packaging [9]. Understanding the diffusion properties of organic molecules in PLA is critical for assessing the transfer of substances from packaging materials into the products. Predictive modeling approaches have been developed to estimate the migration of monomers and additives from packaging into food using diffusion coefficients (D_p). For conventional fossil-based polymers like polyolefins, polystyrene, polyethylene terephthalate, polyamide, etc., such modeling parameters have been well established [10,11]. For these polymers, diffusion modeling can be used to support conformity assessment or product development. Therefore, the migration prediction can support or even greatly simplify the assessment of packaging safety and regulatory compliance. Diffusion coefficients in bio-based polymers are also of interest in other areas such as bioengineering, e.g., in the nanostructure of bone [12], cartilage [13], or the extracellular space of the brain [14]. However, these modeling parameters have not yet been systematically determined for bio-based polymers like PLA. Diffusion modeling parameters are typically derived from migration experiments or experimentally determined D_p , which can be correlated with the molecular weight or molecular volume of the substances. Such correlations enable the prediction of D_p for untested molecules [10,15].

This study aimed to determine the diffusion coefficients of organic substances in PLA using permeation experiments, specifically lag time tests. The tested substances included a range of organic compounds with varying polarity and functional groups. The activation energies of diffusion (E_A) for these molecules were then calculated from the temperature dependence of D_p . From the E_A , the diffusion modeling parameters were derived.

2. Results

2.1. Film Characterization

2.1.1. Differential Scanning Calorimetry (DSC)

The tested PLA films (PLA-S and PLA-N) were characterized for their crystallinity (X_C) and rigid and mobile amorphous fractions (X_{RAF} and X_{MAF} , respectively). Figure 1 shows representative DSC thermograms. As shown in Table 1, all thermal properties of the films, glass transition temperature (T_g), cold crystallization temperature (T_c), and melting temperature (T_m), except for the X_{MAF} percentage, exhibit statistical differences between PLA-S and PLA-N. Both films are predominantly amorphous.

Table 1. Thermal properties of the investigated PLA film samples.

Sample	Thickness, μm	T_g , $^{\circ}\text{C}$	T_c , $^{\circ}\text{C}$	T_{m1} , $^{\circ}\text{C}$	T_{m2} , $^{\circ}\text{C}$	X_C , %	X_{MAF} , %	X_{RAF} , %
PLA-S	20.5 ± 0.6^a	61.3 ± 0.5^a	110.4 ± 1.4^a	160.9 ± 0.4	169.1 ± 0.1^a	3.4 ± 1.1^a	88.3 ± 2.2^a	8.3 ± 2.6^a
PLA-N	30.0 ± 0.9^b	60.1 ± 0.2^b	128.9 ± 1.0^b	n.d.	151.1 ± 0.3^b	1.2 ± 0.2^b	86.6 ± 1.9^a	12.1 ± 0.8^b

Note: n.d. = not detected. Values in the same column with the same lowercase letter are not significantly different based on Tukey's HSD test at a 5% significance level.

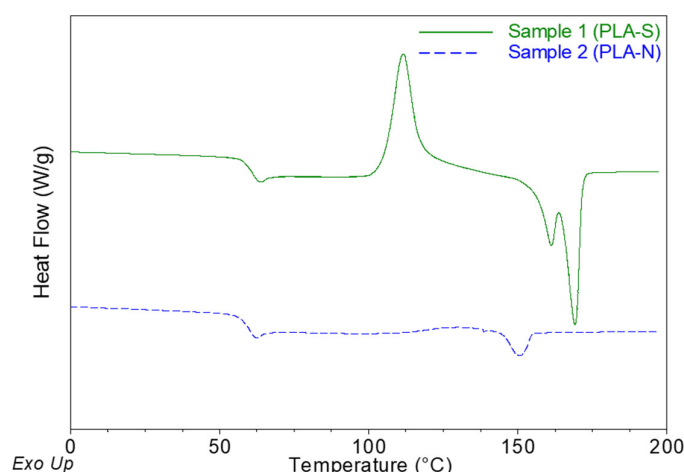


Figure 1. Thermograms of sample 1 (PLA-S) and sample 2 (PLA-N).

2.1.2. Fourier-Transform Infrared (FTIR) Spectroscopy

The FTIR absorbance spectra of PLA-S and PLA-N are provided in the Supplementary Materials (Figures S1–S5). Despite differences in peak intensities, both films' peak positions remain identical, confirming their identical chemical structures. The variations in peak intensities are likely due to differences in film thickness and sample variability.

2.1.3. Gel Permeation Chromatography

Gel permeation chromatography (GPC) was used to determine the molecular weight of the PLA films. Table 2 presents the number average molecular weight (M_n), weight average molecular weight (M_w), and dispersity (D_M) of PLA-S and PLA-N. The D_M values were calculated as M_w/M_n . The M_n values of PLA-S and PLA-N differ significantly, while their M_w values do not.

Table 2. Number average molecular weight (M_n), weight average molecular weight (M_w), and dispersity (D_M) of PLA film samples measured by GPC.

Sample	M_n , kDa	M_w , kDa	D_M
PLA-S	84.5 ± 1.0^a	175.3 ± 0.7^a	2.1 ± 0.02^a
PLA-N	104.4 ± 2.9^b	171.5 ± 3.9^a	1.6 ± 0.04^b

Note: Values in the same column with the same lowercase letters are not significantly different at $\alpha = 0.05$.

2.2. Diffusion Coefficient Determination

The diffusion coefficients (D_p) of organic substances like *n*-alkanes, 1-alcohols, 2-ketones, ethers, esters, amines, and aromatics were determined from the lag time through the two commercial biaxially oriented PLA films, PLA-S and PLA-N. For the 20 μm PLA film (PLA-S), 57 individual D_p were determined. Furthermore, 233 D_p were measured for the 30 μm film (PLA-N). Overall, 290 D_p for 55 organic substances were determined within this study for both investigated PLA films. The D_p were assessed between 20 °C and 90 °C. However, due to the low diffusivity of organic substances in PLA, most of the D_p were measured between 70 °C and 90 °C, above the T_g of PLA, as indicated in Table 3. Only the gaseous alkanes (methane, ethane, and *n*-propane) could be measured at temperatures below the T_g of PLA in a reasonable time. For higher molecular weight substances, the permeation rates for the tested organic compounds were too low and, therefore, below the analytical detection limits of the applied lag time method. The experimentally determined diffusion coefficients are given in the Supplementary Materials (Table S1 for PLA-S and Table S2 for PLA-N). D_p values for the same compounds, such as 1-octanol, 1-butanol, and *n*-hexane for both samples, are comparable and between experimental errors.

Table 3. Results for the activation energies of diffusion and the pre-exponential factor for PLA-S films.

Substance	Molecular Weight, g/mol	Molecular Volume, Å ³	Temperature Range Tested, °C	Number of D_P	Activation Energy E_A , kJ/mol	Pre-Exponential Factor D_0 , cm ² /s
1-propanol	60.1	70.82	70–75	3		
<i>n</i> -pentane	72.2	96.16	70–85	4	230.0	4.11×10^{23}
1-butanol	74.1	87.62	70–85	5	172.6	2.38×10^{15}
<i>n</i> -hexane	86.2	112.96	75–90	4	226.8	6.88×10^{22}
1-pentanol	88.2	104.42	70–85	5	220.4	1.35×10^{22}
<i>n</i> -heptane	100.2	129.77	75–90	4	253.9	4.32×10^{26}
1-hexanol	102.2	121.22	75–85	3		
<i>n</i> -octane	114.2	146.57	75–90	4	279.3	1.56×10^{30}
1-heptanol	116.2	138.03	75–85	3		
<i>n</i> -nonane	128.3	163.37	75–90	4	304.7	6.41×10^{33}
1-octanol	130.2	154.83	75–85	3		
<i>n</i> -decane	142.3	180.17	80–90	3		
<i>n</i> -undecane	156.3	196.97	80–90	3		
<i>n</i> -dodecane	170.3	213.78	80–90	3		
<i>n</i> -tridecane	184.4	230.58	80–90	3		
<i>n</i> -tetradecane	198.4	247.38	80–90	3		

The activation energies of diffusion (E_A) were derived from the temperature dependence of D_P . E_A was only calculated if the following criteria were met to determine the activation energies as accurately as possible: at least four diffusion coefficients were available, showing good linearity in the Arrhenius plot ($r^2 > 0.95$) over at least a 15 °C temperature range. If the temperature range is too small, the slope of the linear correlation in the Arrhenius plot is too inaccurate, and the E_A calculated thereof is consequently also inaccurate. The E_A , as well as the pre-exponential factors, D_0 , are presented in Table 3 for PLA-S and Table 4 for PLA-N.

Table 4. Results for the activation energies of diffusion and the pre-exponential factor for PLA-N films.

Substance	Molecular Weight, g/mol	Molecular Volume, Å ³	Temperature Range Tested, °C	Number of D_P	Activation Energy E_A , kJ/mol	Pre-Exponential Factor D_0 , cm ² /s
methane	16.0	28.64	20	1		
ethane	30.1	45.76	20–60	4	60.6	1.47×10^0
<i>n</i> -propane	44.1	62.56	50–70	3		
acetone	58.1	64.74	60–75	5	114.5	3.02×10^7
<i>n</i> -butane	58.1	79.36	70	1		
methyl formate	60.1	57.16	60–70	3		
1-propanol	60.1	70.82	65–80	4	162.0	2.81×10^{14}
pyrrole	67.1	69.03	70	1		
cyclopentane	70.1	85.80	70–85	4	247.0	1.41×10^{26}
tetrahydrofuran	72.1	77.98	70–85	4	191.3	1.73×10^{18}
2-butanone	72.1	81.54	60–85	10	160.7	9.09×10^{13}
<i>n</i> -pentane	72.2	96.16	70–85	9	239.4	1.92×10^{25}
1,3-dioxolane	74.1	70.17	60–85	6	141.4	1.47×10^{11}
ethyl formate	74.1	73.97	60–75	4	128.7	3.87×10^9
1-butanol	74.1	87.62	65–85	5	205.0	2.96×10^{20}
benzene	78.1	84.04	70–85	4	212.8	2.45×10^{21}
pyridine	79.1	79.89	70	1		
cyclopentanone	84.1	87.98	70–85	4	242.2	2.93×10^{25}
cyclohexane	84.2	102.60	75–85	3		
2-pentanone	86.1	98.34	65–80	5	256.6	1.10×10^{28}
<i>n</i> -hexane	86.2	112.96	75–85	8		
2-methyl-1,3-dioxolane	88.1	86.75	65–80	4	228.4	5.77×10^{23}
1,4-dioxane	88.1	86.97	70–85	3		
<i>n</i> -propyl formate	88.1	90.77	60–80	5	191.9	3.60×10^{18}
1-pentanol	88.2	104.42	70–85	4	219.3	2.43×10^{22}
toluene	92.1	100.61	70–85	3	236.6	4.81×10^{24}
aniline	93.1	95.33	70	1		

Table 4. Cont.

Substance	Molecular Weight, g/mol	Molecular Volume, Å ³	Temperature Range Tested, °C	Number of D_P	Activation Energy E_A , kJ/mol	Pre-Exponential Factor D_0 , cm ² /s
cyclohexanone	98.1	104.79	75–85	3		
2-hexanone	100.2	115.15	70–85	5	238.2	1.02×10^{25}
<i>n</i> -heptane	100.2	129.77	75–90	9	278.9	5.12×10^{30}
<i>n</i> -butyl formate	102.1	107.57	65–80	4	247.1	3.29×10^{26}
1-hexanol	102.2	121.22	70–85	4	241.0	2.53×10^{25}
ethylbenzene	106.2	117.41	70–90	5	246.0	6.78×10^{25}
4-vinyl cyclohexene	108.2	124.17	75–90	4	246.4	4.31×10^{25}
2-heptanone	114.2	131.95	70–85	5	261.4	2.05×10^{28}
<i>n</i> -octane	114.2	146.57	80–90	6		
<i>n</i> -pentyl formate	116.2	124.37	70–80	3		
1-heptanol	116.2	138.03	70–85	4	267.5	1.66×10^{29}
<i>n</i> -propylbenzene	120.2	134.21	75–90	4	230.2	2.44×10^{23}
naphthalene	128.2	128.03	75–90	4	236.3	1.56×10^{24}
2-octanone	128.2	148.75	75–85	4		
<i>n</i> -nonane	128.3	163.37	80–90	6		
<i>n</i> -hexyl formate	130.2	141.17	70–80	3		
1-octanol	130.2	154.83	70–85	4	279.4	7.62×10^{30}
<i>n</i> -butylbenzene	134.2	151.01	75–90	4	242.3	1.21×10^{25}
methyl naphthalene	142.2	144.60	75–90	4	258.0	1.35×10^{27}
<i>n</i> -decane	142.3	180.17	80–90	6		
<i>n</i> -heptyl formate	144.2	157.97	75–80	2		
ethyl naphthalene	156.2	161.40	75–90	4	266.2	1.75×10^{28}
<i>n</i> -undecane	156.3	196.97	80–90	6		
<i>n</i> -dodecane	170.3	213.78	80–90	6		
<i>n</i> -tridecane	184.4	230.58	80–90	6		
<i>n</i> -tetradecane	198.4	247.38	80–90	6		
di-iso-propyl naphthalene	212.3	227.94	80–90	3		

3. Discussion

The experimentally determined D_P values for the 55 individual molecules of different polarity, functional groups, as well as molecular size, can be considered as representative of typical permeants of migrants of PLA. In general, large molecules diffuse slower through a polymer matrix compared with smaller molecules of a similar structure. As expected, higher molecular volume V results in lower D_P at a given temperature. Moreover, higher temperature results in higher D_P , which is expected from an Arrhenius relationship. However, due to the low diffusivity of PLA, the largest molecule tested in this study was di-*iso*-propyl naphthalene, with a molecular weight of 212.3 g/mol (molecular volume 227.94 Å³). Larger molecules therefore diffuse very slowly in the polymer so that the lag time is very long. For example, the lag time of di-*iso*-propyl naphthalene at 80 °C and 20 µm film is about 3 days. At the lower temperature of 60 °C, the lag time of di-*iso*-propyl naphthalene increases to approximately 18 years, as predicted for the diffusion modeling approach established in this study. We can assume a thinner PLA film of 10 µm will decrease the lag time to about 4.5 years, but this is still too long for an experimental determination of the lag time. In addition, thin films of 10 µm are not commercially available. The experimental measurement window is therefore very limited and is a condition determined by molecule size, film thickness, and temperature. Furthermore, due to the low diffusivity of PLA, almost all D_P in this study were measured above the glass transition temperature, where the PLA is in the rubbery state. This means that the diffusion is higher than in the glassy state and is an additional overestimating factor for predicting the migration below T_g .

As a result, the experimentally determined D_P show a very strong dependence on the temperature. The E_A were calculated from this dependence. The E_A and the D_0 values for each permeant were calculated from the Arrhenius relationship below or above T_g . The

results show good linearity for the investigated permeants, indicating that the diffusion process follows Fick's laws of diffusion. Figure 2 shows the correlations between E_A and the molecular volume V , as well as between E_A and the pre-exponential factor D_0 , respectively. The experimental data for PLA are shown in comparison with the published activation energy data for polyester PET [15] and PEN [16]. For all three polyester polymers, the E_A values are in the same order of magnitude for small molecules up to V of approximately $100 \text{ \AA}^3$ and for E_A of about 120 kJ/mol . For larger molecules, the E_A values for PLA are significantly higher than those of PET and PEN. The D_0 values for all three polyesters follow a strong linear relationship over the range of approximately 20 orders of magnitude for PET and PEN, and approximately 40 orders of magnitude for PLA. The slope of the E_A and D_0 correlation for PLA is different from the slopes determined for PET and PEN. Compared to PET and PEN, the increase in activation energy with molecule size is significantly more substantial for PLA. This means that even small molecules exhibit high activation energies of diffusion. A high activation energy implies that the temperature has a much stronger influence on diffusion. Therefore, increasing temperature has a high influence on the migration of substances into food or food simulants. This increase is not as significant for PET and PEN. However, like PET and PEN, PLA is a low-diffusible polymer which only releases substances into the food in small quantities unless high-swelling food simulants are used.

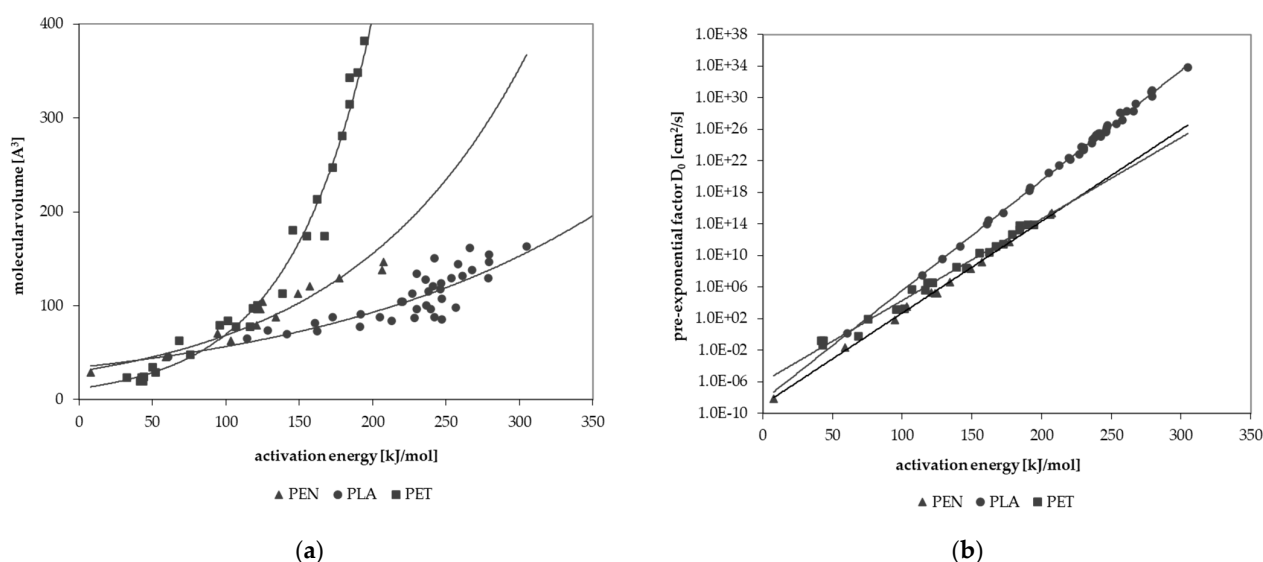


Figure 2. Correlations between the activation energy of diffusion E_A and the molecular volume V of the test permeants (a), and correlations between E_A and the pre-exponential factor, D_0 (b), for PLA (this study), PET [15], and PEN [16].

The two correlations can be used to determine the diffusion modeling parameters for PLA for Equation (1). This equation was developed for PET [15] but also applies to PLA, and the correlations can be established for PLA as well (Figure 2). According to Equation (1), the D_p can be predicted from the molecular volume V with the diffusion modeling parameters a to d for PLA. The parameters a to d are the slope and the axis intercept, respectively, in the two correlations for PLA. The parameter a is the slope of the correlation between pre-exponential factors D_0 and E_A , with b being the intercept of this correlation. Parameters c and d are the intercept and slope of the correlation between V and E_A . The diffusion modeling parameters derived from the two correlations are

given in Table 5 along with the previously reported values for PET [15] and PEN [16]. In Equation (1), V is the molecular volume and T is the temperature in Kelvin.

$$D_P = b \left(\frac{V}{c} \right)^{\frac{a-1}{d}} \quad (1)$$

Table 5. Diffusion modeling parameters for PLA from Equation (1) compared to published values for PET and PEN.

Parameter	PLA	PET ^a	PEN ^b
a [1/K]	2.67×10^{-3}	1.93×10^{-3}	2.23×10^{-3}
b [cm ² /s]	4.46×10^{-9}	2.37×10^{-6}	1.12×10^{-9}
c [Å ³]	34.4	11.1	31.1
d [1/K]	4.14×10^{-5}	1.50×10^{-4}	6.74×10^{-5}

^a Values reported in [15]; ^b values reported in [16].

Figure 3 shows a comparison of the experimentally determined D_P with the predicted D_P from Equation (1) and the parameters a to d from Table 5. As a result, the slope of the correlation is near 1 and the straight line almost passes through the origin, which indicates the D_P were predicted realistically and well over the molecular size and temperature range. However, there is a certain spread in the data of experimentally determined D_P versus predicted D_P , possibly due to slight differences among the PLA-S and PLA-N films. The two dashed lines represent the 95% confidence interval of the correlation. Previously, it has been shown that not only the crystallinity of the films—in this case, both mostly amorphous—but also the X_{RAF} , albeit small compared with X_{MAF} , and M_n play a role in D_P [17,18].

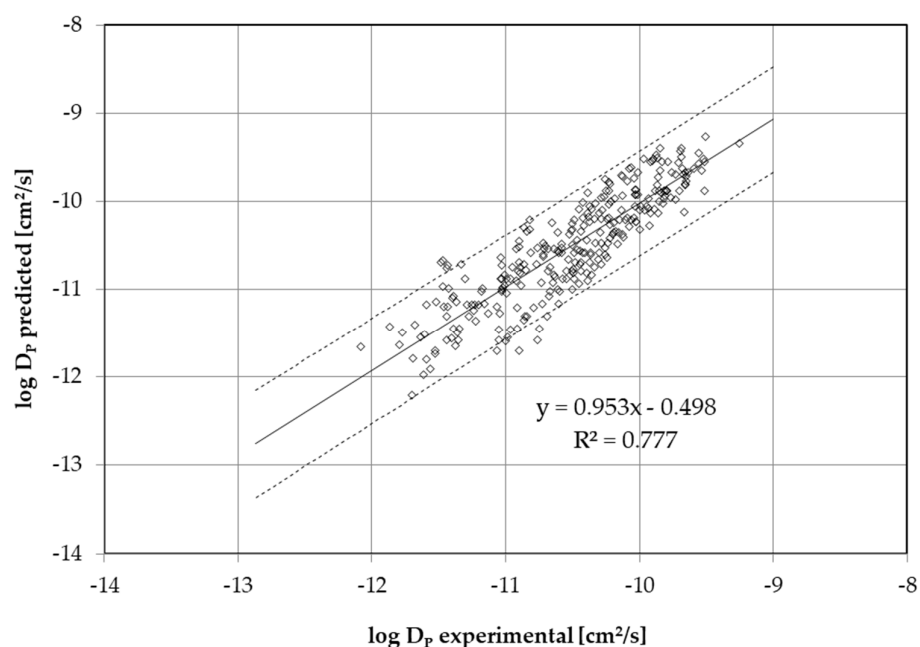


Figure 3. Log–log plot of the experimental and predicted diffusion coefficients for PLA. Dashed lines represent the 95% confidence interval.

A comparison of the experimentally determined diffusion coefficients with data from the literature [2] is very difficult. On the one hand, there is very little data available. Secondly, the permeation rates were mostly determined while the diffusion coefficients were not. However, the few D_P measured previously are generally higher than the D_P

measured in this study. It is very likely the permeation is measured at higher concentrations, which leads to interactions between the permeant and the polymer in the case of PLA, which probably increases the measured D_p .

4. Materials and Methods

4.1. Materials

Two commercial biaxially oriented PLA films were used in this study:

- PLA-S: A 20- μm biaxially oriented PLA film (Evlon[®], BI-AX International Inc., Wingham, ON, Canada).
- PLA-N: A 30- μm biaxially oriented PLA film (Nativia[®], Taghleef Industries, Newark, DE, USA).

4.2. Film Characterization

4.2.1. Differential Scanning Calorimetry (DSC)

A differential scanning calorimeter, Q100 (TA Instruments, New Castle, DE, USA), calibrated with indium standards, was used for characterization and investigation of the crystallinity of the films. The film samples, 5–10 mg, were weighed and sealed in an aluminum pan, and the thermal analyses were performed in nitrogen atmosphere with a flow rate of 70 mL/min. For film characterization, the samples were cooled from room temperature to $-50\text{ }^{\circ}\text{C}$, heated from -50 to $200\text{ }^{\circ}\text{C}$ (first heating cycle), maintained isothermally for 1 min at $200\text{ }^{\circ}\text{C}$, cooled until $-50\text{ }^{\circ}\text{C}$, and finally heated to $200\text{ }^{\circ}\text{C}$ (second heating cycle). The temperature ramp rate for all the cycles was $10\text{ }^{\circ}\text{C}/\text{min}$. The characterization for each film was run in triplicate and the results were analyzed with the TA Instruments Universal Analysis 2000 software version 4.5A to determine the T_g , T_c , and T_m , as well as the enthalpies associated with these temperatures based on results from the second heating cycle. The degree of crystallinity (X_C) was calculated from Equation (2):

$$X_C = \frac{\Delta H_m - \Delta H_c}{\Delta H_f^0} \quad (2)$$

where ΔH_m and ΔH_c are the enthalpy of melting and the enthalpy of cold crystallization of the sample, respectively. ΔH_f^0 is the enthalpy of fusion of pure crystalline sample, which is 93.1 J/g for PLA [19]. The mobile amorphous fraction (X_{MAF}) was calculated from Equation (3):

$$X_{MAF} = \frac{\Delta C_p}{\Delta C_p^0} \quad (3)$$

where ΔC_p and ΔC_p^0 are the changes in heat capacity at T_g for the semicrystalline sample and the fully amorphous sample, respectively. ΔC_p^0 for a fully amorphous PLA is $0.639\text{ J}/(\text{g }^{\circ}\text{C})$ [20]. The rigid amorphous fraction (X_{RAF}) was calculated from Equation (4):

$$X_{RAF} = 1 - X_C - X_{MAF} \quad (4)$$

4.2.2. Fourier-Transform Infrared Spectroscopy

Chemical functional groups in the films were identified using Fourier-transform infrared (FTIR) spectroscopy (IRAffinity-1S, Shimadzu, Columbia, MD, USA) in both transmittance and attenuated total reflectance (ATR) modes. Each spectrum was recorded with a resolution of 2 per cm and a mirror speed of 2.8 mm/s , with a total of 20 scans per measurement.

4.2.3. Gel Permeation Chromatography

Molecular weight distribution was determined by gel permeation chromatography (GPC) using a Waters 1515 system (Waters, Milford, MA, USA) equipped with a refractive index detector (Waters 2414) and HR Stryragel[®] columns of 7.8 mm × 300 mm (HR4, HR3, and HR2). Approximately 10 mg of PLA was dissolved in 5 mL of tetrahydrofuran (THF) (Pharmco-Aaper, Brookfield, CT, USA), filtered through a 0.45 µm PTFE filter (Simsii, Inc., Port Irvine, CA, USA), and injected into a 2 mL GPC glass vial. All GPC runs were eluted with THF at a flow rate of 1.0 mL/min at 35 °C for 50 min and an injection volume of 100 µL. A calibration curve was constructed using polystyrene standards with the Mark–Houwink constants $K = 0.0164$ mL/g and $\alpha = 0.704$. Data were analyzed using Waters Breeze2[®] software version 3.30. Each sample was analyzed in triplicate.

4.2.4. Statistical Analysis

Statistical analyses of DSC and GPC data were performed by one-way analysis of variance (ANOVA), followed by Tukey's multiple comparison test at a 95% confidence level ($\alpha = 0.05$) using SAS[®] Studio Release 3.8 (SAS Institute Inc., Cary, NC, USA).

4.3. Diffusion Coefficient Determination

4.3.1. Permeants

Two types of permeants were tested: liquid permeants and permanent gases.

- Liquid permeants: *n*-alkanes (*n*-pentane to *n*-tetradecane), 1-alcohols (1-propanol to 1-octanol), 2-ketones (acetone to 2-octanone), cyclic alkanes, ethers, ketones (tetrahydrofuran, cyclohexane, 4-vinylcyclohexene, 1,3-dioxolane, 2-methyl-1,3-dioxolane, 1,4-dioxane, cyclopentane, cyclopentanone, cyclohexanone), esters (formic acid methyl ester to formic acid heptyl ester), amines (pyridine, pyrrol, 2,6-lutidine, aniline, 2-aminobenzonitrile), and aromatic substances (benzene, toluene, ethylbenzene, *n*-propylbenzene, *n*-butylbenzene, naphthalene, 1-methylnaphthalene, 1-ethylnaphthalene, 2,7-di-*iso*-propylnaphthalene, phenanthrene, anthracene). The respective groups of substances were mixed and measured together.
- Permanent gases: Methane, ethane, *n*-propane, and *n*-butane were tested as a mixture of gaseous alkanes.

4.3.2. Permeation Cell

PLA films were clamped in a permeation steel cell between two sealant rings. The surface area of the tested films was 191 cm². The permeation cell, placed in a climate chamber, was divided into a lower and an upper space by the film. The lower space had a volume of 7667 cm³. The permeants were introduced into the cell as follows:

- Liquid permeants: The liquid mixtures were injected into the lower space of the permeation cell through a septum using a syringe. Upon injection, the permeants evaporated immediately at high temperatures (65 °C to 90 °C).
- Permanent gases: The gaseous alkane mixture was flushed through the lower space of the permeation cell with a constant gas flow.

The upper space of the permeation cell was permanently rinsed with a pure stream of nitrogen (20 mL/min) which moved the permeated substances out of the cell. The nitrogen stream went through a connected enrichment unit and the permeants were trapped on this unit over a period of 20 min. The enrichment unit was connected to a gas chromatograph (GC) with flame ionization detection. The permeants were directly desorbed into the GC, where their quantities were determined through quantitative analysis. During the GC run, the next sample was trapped on the enrichment unit and subsequently injected into the GC. By using this method, one kinetic point was measured every 45 min.

Gas Chromatographic conditions for the different permeants were as follows:

- Liquid permeants: Column: Rxi 624, length: 60 m, internal diameter: 0.32 mm, film thickness: 1.8 μm , carrier gas: 120 kPa helium. Temperature program: 40 $^{\circ}\text{C}$ (2 min), rate 10 $^{\circ}\text{C}/\text{min}$ to 200 $^{\circ}\text{C}$, rate 20 $^{\circ}\text{C}/\text{min}$ to 270 $^{\circ}\text{C}$, and held for 8 min. Pre-trap: substances collected on 20 mm length by 5 mm diameter of Carbopack B, desorbed at 350 $^{\circ}\text{C}$. Main trap: substances focused at -46°C on 30 mm length by 1.4 mm diameter of Carbopack B, desorbed at 320 $^{\circ}\text{C}$.
- Permanent gases: Column: Poraplot Q, length: 30 m, internal diameter: 0.53 mm, film thickness: 20 μm , carrier gas: 120 kPa helium. Temperature program: 70 $^{\circ}\text{C}$ (0.5 min), rate 30 $^{\circ}\text{C}/\text{min}$ to 150 $^{\circ}\text{C}$, and held for 5 min. Pre-trap: substances collected on 20 mm length by 5 mm diameter of Carbopack B, desorbed at 350 $^{\circ}\text{C}$. Main trap: substances focused at -46°C on 30 mm length by 1.4 mm diameter of active charcoal 140–280 μm , desorbed at 320 $^{\circ}\text{C}$.

4.3.3. Diffusion Coefficient Calculation

Isostatic and quasi-isostatic methods are often used to determine the permeation of organic substances through films [21]. In these methods, a film is clamped in a permeation cell and brought into contact with a known concentration of the permeant on one side. The permeated quantity is purged with an inert carrier gas and brought for quantification, if necessary after concentration, to the detector. The lag time is the intersection of the x -axis of the tangent to the steady-state concentrations. The lag time can be used to calculate the D_p according to Equation (5) [2]. Calibration was performed with injections of the applied permeants at known amounts. The diffusion coefficients D_p (in cm^2/s) were calculated from the lag times (in s) according to Equation (5), where l is the film thickness (in cm). The activation energies of diffusion E_A were calculated from the D_p at various temperatures according to the Arrhenius equation (Equation (6)) below or above T_g , where D_0 is the pre-exponential factor, R is the gas constant, and T is the temperature in Kelvin.

$$\text{lag time} = \frac{l^2}{6D_p} \quad (5)$$

$$D_p = D_0 e^{-\frac{E_A}{RT}} \quad (6)$$

4.3.4. Molecular Volume Calculations

The molecular volumes were calculated using the freely accessible program Molinspiration [22]. The program calculates the molecular volumes using a group-based contribution method.

5. Conclusions

In this study, a total of 290 diffusion coefficients were experimentally determined from the lag times of the various substances during permeation through PLA. From this, 38 activation energies of diffusion were calculated. The diffusion coefficients D_p as well as the activation energies of diffusion E_A correlate well with the molecular volume V of the permeants. The pre-exponential factors D_0 also correlate with the E_A . If other molecules are following such correlations, the D_p and E_A of other substances in PLA can be predicted from the V . The data are used to establish the diffusion modeling parameters for PLA. These modeling parameters can now be used to predict both the permeation of organic substances through PLA and the migration of monomers, additives, or other substances from PLA. The D_p determined in this study are actual diffusion coefficients. However, in migration studies, which are usually carried out in food simulants, other effects such as swelling of

the packaging surface may occur, which increase diffusion and thus migration [8,23,24]. In real foods, however, such swelling effects occur less frequently.

Furthermore, the prediction of migration using diffusion modeling should always be overestimated [11,25]. The overestimation factor in D_p predicted from Equation (1) and the modeling parameters in Table 5 are 1.3 on average (median 1.0). The D_p are therefore predicted very well from the diffusion parameters a to d and Equation (1). This is shown in the log–log plot (Figure 3), which shows a slope near 1 and where the correlation line runs almost completely through the origin. At the same time, however, this means that almost half of the D_p underestimate the migration or permeation. To achieve a slight overestimation, the molecule size can be virtually reduced to predict higher diffusion coefficients. Based on the experimental data, a 30% molecular size reduction appears sufficient as a worst-case scenario. This reduction of the molecular volume by 30% results in a mean overestimation factor of 9.2 (median 4.6). In practice, this appears to be a good overestimation factor for predicting the D_p with a sufficient overestimation of the actual migration. This means the overestimation factor in migration is about 3, because the diffusion coefficient correlates with the square root of the migration.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules30092064/s1>, Figures S1–S5—FTIR analyses. Figure S6—correlation of determined D_p with molecular volume compared to predicted D_p . Tables S1 and S2—Diffusion coefficients.

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References

1. Lim, L.-T.; Auras, R.; Rubino, M. Processing technologies of poly(lactic acid). *Prog. Polym. Sci.* **2008**, *33*, 820–852. [CrossRef]
2. Sonchaeng, U.; Iniguez-Franco, F.; Auras, R.; Selke, S.; Rubino, M.; Lim, L.-T. Poly(lactic acid) mass transfer properties. *Prog. Polym. Sci.* **2018**, *86*, 85–121. [CrossRef]
3. Ewender, J.; Welle, F. Determination and prediction of the lag-times of hydrocarbons through a PET film. *Packag. Technol. Sci.* **2014**, *27*, 963–974. [CrossRef]
4. Macnamara, J.F., Jr.; Vallery, R.; Gidley, D.; Auras, R. Density and crystallinity correlations: Enhancing moisture barrier properties in poly(L-lactic acid), poly(D-lactic acid), and stereocomplex-poly(L,D-lactic acid) films. *J. Appl. Polym. Sci.* **2025**, e56986. [CrossRef]
5. Bradley, E.L. Biobased Materials Used in Food Contact Applications: An Assessment of the Migration Potential. Report of the Food and Environment Research Agency, York (2010). Available online: <https://www.food.gov.uk/sites/default/files/media/document/a03070.pdf> (accessed on 6 April 2025).
6. Aznar, M.; Ubeda, S.; Dreolin, N.; Nerin, C. Determination of non-volatile components of a biodegradable food packaging material based on polyester and poly-lactic acid (PLA) and its migration to food simulants. *J. Chromatogr. A* **2019**, *1583*, 1–8. [CrossRef] [PubMed]

7. Ubeda, S.; Aznar, M.; Alfaro, P.; Nerin, C. Migration of oligomers from a food contact biopolymer based on polylactic acid (PLA) and polyester. *Anal. Bioanal. Chem.* **2019**, *411*, 3521–3532. [CrossRef] [PubMed]
8. Mutsuga, M.; Kawamura, Y.; Tanamoto, K. Migration of lactic acid, lactide and oligomers from polylactide food-contact materials. *Food Addit. Contam. Part A* **2008**, *25*, 1283–1290. [CrossRef] [PubMed]
9. Ubeda, S.; Aznar, M.; Nerin, C. Determination of volatile compounds and their sensory impact in a biopolymer based on polylactic acid (PLA) and polyester. *Food Chem.* **2019**, *294*, 171–178. [CrossRef] [PubMed]
10. Begley, T.; Castle, L.; Feigenbaum, A.; Franz, R.; Hinrichs, K.; Lickley, T.; Mercea, P.; Milana, M.-R.; O'Brien, A.; Rebre, S.; et al. Evaluation of migration models that might be used in support of regulations for food-contact plastics. *Food Addit. Contam.* **2005**, *22*, 73–90. [CrossRef] [PubMed]
11. Practical Guidelines on the Application of Migration Modelling for the Estimation of Specific Migration, EU Report 27529 EN, ISBN 978-92-79-52790-6. 2015. Available online: <https://op.europa.eu/de/publication-detail/-/publication/1b79bc61-97f6-11e5-983e-01aa75ed71a1> (accessed on 6 April 2025).
12. Bini, F.; Pica, A.; Marinozzi, A.; Marinozzi, F. 3D random walk model of diffusion in human hypo- and hyper-mineralized collagen fibrils. *J. Biomech.* **2021**, *125*, 110586. [CrossRef] [PubMed]
13. Momot, K.I. Diffusion tensor of water in model articular cartilage. *Eur. Biophys. J.* **2011**, *40*, 81–91. [CrossRef] [PubMed]
14. Jin, S.; Zador, Z.; Verkman, A.S. Random-walk model of diffusion in three dimensions in brain extracellular space: Comparison with microfiberoptic photobleaching measurements. *Biophys. J.* **2008**, *95*, 1785–1794. [CrossRef] [PubMed]
15. Welle, F. A new method for the prediction of diffusion coefficients in poly(ethylene terephthalate). *J. Appl. Polym. Sci.* **2013**, *129*, 1845–1851. [CrossRef]
16. Ewender, J.; Welle, F. Diffusion coefficients of n-alkanes and 1-alcohols in polyethylene naphthalate (PEN). *Int. J. Polym. Sci.* **2019**, *2019*, 2748649. [CrossRef]
17. Guinault, A.; Sollogoub, C.; Ducruet, V.; Domenek, S. Impact of crystallinity of poly(lactide) on helium and oxygen barrier properties. *Eur. Polym. J.* **2012**, *48*, 779–788. [CrossRef]
18. Piringier, O.G.; Baner, A.L. (Eds.) *Plastic Packaging—Interactions with Food and Pharmaceuticals*; Wiley-VCH: Weinheim, Germany, 2008; ISBN 978-3-527-31455-3.
19. Fischer, E.W.; Sterzel, H.J.; Wegner, G. Investigation of the structure of solution grown crystals of lactide copolymers by means of chemical reactions. *Kolloid-Z. Z. Polym.* **1973**, *251*, 980–990. [CrossRef]
20. Magon, A.; Pyda, M. Study of crystalline and amorphous phases of biodegradable poly(lactic acid) by advanced thermal analysis. *Polymer* **2009**, *50*, 3967–3973. [CrossRef]
21. Selke, S.E.M.; Culter, J.D. *Plastics Packaging: Properties, Processing, Applications, and Regulations*, 3rd ed.; Hanser Publications: Cincinnati, OH, USA, 2016; ISBN 978-1-56990-443-5.
22. Molinspiration. Available online: www.molinspiration.com (accessed on 30 April 2025).
23. Kirchkeszner, C.; Petrovics, N.; Tabi, T.; Magyar, N.; Kovacs, J.; Szabo, B.S.; Nyiri, Z.; Eke, Z. Swelling as a promoter of migration of plastic additives in the interaction of fatty food simulants with polylactic acid and polypropylene-based plastics. *Food Control* **2022**, *132*, 108354. [CrossRef]
24. Dragan, V.K.; Petrovics, N.; Kirchkeszner, C.; Tabi, T.; Szabo, B.S.; Eke, Z. The kinetics of swelling and migration: A case study of plasticized polylactic acid food contact plastics tested with ethanolic food simulants. *Express Polym. Lett.* **2024**, *18*, 391–405. [CrossRef]
25. Regulation No. 10/2011 of 14 January 2011 on Plastic Materials and Articles Intended to Come into Contact with Food. Official Journal of the European Union L12/1. Available online: <https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32011R0010&from=EN> (accessed on 6 April 2025).

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