CRITICAL AND SYSTEMATIC REVIEW OF POLY(LACTIC ACID) MASS TRANSFER AND EVALUATION OF THE *IN-SITU* CHANGES OF ITS THERMO-MECHANICAL PROPERTIES WHEN IMMERSED IN ALCOHOL SOLUTIONS

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ABSTRACT

CRITICAL AND SYSTEMATIC REVIEW OF POLY(LACTIC ACID) MASS TRANSFER AND EVALUATION OF THE *IN-SITU* CHANGES OF ITS THERMO-MECHANICAL PROPERTIES WHEN IMMERSED IN ALCOHOL SOLUTIONS

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Properties of poly(lactic acid) (PLA) are affected by environmental conditions such as temperature, humidity, and chemical exposure. Mass transport of gases, vapors, and organic compounds in PLA is a concern when designing applications since PLA is permeable to them. Even though mass transfer parameters of PLA such as permeability, diffusion, and solubility coefficients have been reported in the literature, the values and units are scattered and inconsistent and most of the analyses only consider PLA as a two-phase structure consisting of a crystalline and an amorphous phase. The recent concept of the three-phase model that separates the amorphous phases into the mobile and rigid amorphous fractions has barely been considered when assessing PLA's mass transfer properties. Besides gases and vapors, PLA may also interact with solvents and aqueous solutions. Literature on PLA properties "after" being contacted with solvents and solutions is scarce. Only a limited number of studies reported properties of PLA "during" immersion (i.e., *in-situ*). Thus, this dissertation aims to: 1) provide a comprehensive, systematic, and critical review of mass transfer properties of PLA and PLA-based materials such as blends and composites, along with review of migration of chemical compounds from PLA, and 2) evaluate the *in-situ* changes in thermo-mechanical properties of PLA when in contact with alcohol solutions using a dynamic mechanical analysis technique. The literature review shows that PLA

provides moderate barrier to gases, water vapor, and organic vapors and that PLA barrier can be enhanced through modification such as blending with other polymers. The *in-situ* immersion of PLA in alcohol solutions showed reductions in PLA's glass transition temperatures (T_g) during immersion when compared to the T_g of dry PLA. The T_g reductions became smaller as the number of carbon atoms in aliphatic alcohols C1– C10 increased. Immersion in 50% (v/v) 2-propanol resulted in a T_g that was higher than when PLA was immersed in 100% 2-propanol but lower than when PLA was immersed in water, implying that the concentrations of the solvents affect the changes in PLA's T_{g} . The chemical isomerism in propanol (i.e., 1- and 2-propanol) did not affect the T_g reduction. The Flory-Huggins interaction parameters and the Hansen solubility parameters were used to explain the reduction in T_g of PLA based on the interactions of PLA with the alcohol solutions. The relationship explained the interactions between PLA and alcohols with small molecules (C1–C8), but bigger alcohols (C9–C10) did not fit the prediction. Overall, the experimental results are not yet sufficient to predict the T_g reduction of PLA in other solvents. Further research on the mass transfer properties of PLA is needed for PLA to reach its full commercial potential.

To my family and friends, and my mentors, teachers and professors.

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KEY TO SYMBOLS AND ABBREVIATIONS

α	thermal expansion coefficients
a*	an empirical factor for interaction parameter
	calculation
δ_d	Hansen solubility parameter based on the
	contributions from the dispersion
δ_h	Hansen solubility parameter based on the
	contributions from the hydrogen bond
$\delta_{ ho}$	Hansen solubility parameter based on the
	contributions from the polar bond
ΔH_C	heat of condensation
ΔH_M	heat of mixing
ΔHs	heat of sorption
X 12	interaction parameter
AP	amylopectin
ATBC	acetyl tributyl citrate
aw	water activity
ВНА	butylated hydroxyanisole
BHT	butylated hydroxytoluene
Biophan	PLA from Treofan
C30B	Cloisite® 30B

CA-PBSA	crotonic acid functionalized poly(lactic acid) coupling
	poly(butylene succinate-co-adipate)
CF	crystalline fraction
D	diffusion coefficient
Dcio ₂	diffusion coefficient of chlorine dioxide (gas)
D _{CO2}	diffusion coefficient of carbon dioxide (gas)
<i>D</i> _{H2} о	diffusion coefficient of water vapor
DMA	dynamic mechanical analysis
D _{O2}	diffusion coefficient of oxygen (gas)
DS	degree of swelling
DSC	differential scanning calorimetry
ED	activation energy of diffusion
E _{D,CO2}	activation energy of diffusion of carbon dioxide (gas)
E_{D,O_2}	activation energy of diffusion of oxygen (gas)
Ep	activation energy of permeation
E _{P,CH4}	activation energy of permeation of methane (gas)
EP,CIO2	activation energy of permeation of chlorine dioxide
	(gas)
E _{P,CO2}	activation energy of permeation of carbon dioxide
	(gas)
E _{P,H2}	activation energy of permeation of hydrogen (gas)
<i>Е</i> _{Р,H2} 0	activation energy of permeation of water vapor

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E _{P,N2}	activation energy of permeation of nitrogen (gas)
E _{P,O2}	activation energy of permeation of oxygen (gas)
EVLON	PLA film from BI-AX International Inc.
EVOH	ethylene vinyl alcohol
FH	Flory-Huggins
FTIR-ATR	Fourier transform infrared spectroscopy-attenuated
	total reflection
FV	free volume
HDPE	high density polyethylene
HSP	Hansen solubility parameters
IGC	inverse gas chromatography
κ	partition coefficient
K _{p,f}	partition coefficient of solute between polymer p and
	liquid f
LA	lactic acid
LDH	layered double hydroxide
LDPE	low density polyethylene
MAF	mobile amorphous fraction
MMT	montmorillonite
Mn	number-average molecular weight
M _w	weight-average molecular weight
MSB	magnetic suspension balance
NS	nanosilica

o-LA	lactic acid oligomer
OPLA	oriented poly(lactic acid)
OMMT	organically-modified montmorillonite
Р	permeability coefficient
PAN	polyacrylonitrile
PBSA	poly(butylene succinate-co-adipate)
PC	polycarbonate
P _{CH4}	permeability coefficient of methane (gas)
PCL	polycaprolactone
P _{ClO₂}	permeability coefficient of chlorine dioxide (gas)
P _{CO2}	permeability coefficient of carbon dioxide (gas)
PDLA	PLA with isotactic sequences of D-lactide
PDLA PDLLA	PLA with isotactic sequences of D-lactide PLA formed by <i>meso</i> -lactide (D,L) or a mixture of L-
PDLA PDLLA	PLA with isotactic sequences of D-lactide PLA formed by <i>meso</i> -lactide (D,L) or a mixture of L- and D-lactides, or PLA polymerized from a racemic
PDLA PDLLA	PLA with isotactic sequences of D-lactide PLA formed by <i>meso</i> -lactide (D,L) or a mixture of L- and D-lactides, or PLA polymerized from a racemic mixture (50:50) of L- and D-lactides
PDLA PDLLA PE	PLA with isotactic sequences of D-lactide PLA formed by <i>meso</i> -lactide (D,L) or a mixture of L- and D-lactides, or PLA polymerized from a racemic mixture (50:50) of L- and D-lactides polyethylene
PDLA PDLLA PE PEG	PLA with isotactic sequences of D-lactide PLA formed by <i>meso</i> -lactide (D,L) or a mixture of L- and D-lactides, or PLA polymerized from a racemic mixture (50:50) of L- and D-lactides polyethylene poly(ethylene glycol)
PDLA PDLLA PE PEG PEN	PLA with isotactic sequences of D-lactide PLA formed by <i>meso</i> -lactide (D,L) or a mixture of L- and D-lactides, or PLA polymerized from a racemic mixture (50:50) of L- and D-lactides polyethylene poly(ethylene glycol) poly(ethylene naphthalate)
PDLA PDLLA PE PEG PEN PET	PLA with isotactic sequences of D-lactide PLA formed by <i>meso</i> -lactide (D,L) or a mixture of L- and D-lactides, or PLA polymerized from a racemic mixture (50:50) of L- and D-lactides polyethylene poly(ethylene glycol) poly(ethylene naphthalate) poly(ethylene terephthalate)
PDLA PDLLA PE PEG PEN PET PG	PLA with isotactic sequences of D-lactide PLA formed by <i>meso</i> -lactide (D,L) or a mixture of L- and D-lactides, or PLA polymerized from a racemic mixture (50:50) of L- and D-lactides polyethylene poly(ethylene glycol) poly(ethylene naphthalate) poly(ethylene terephthalate) propyl gallate
PDLA PDLLA PE PEG PEN PET PG PH2	PLA with isotactic sequences of D-lactide PLA formed by <i>meso</i> -lactide (D,L) or a mixture of L- and D-lactides, or PLA polymerized from a racemic mixture (50:50) of L- and D-lactides polyethylene poly(ethylene glycol) poly(ethylene naphthalate) poly(ethylene terephthalate) propyl gallate permeability coefficient of hydrogen (gas)

P _{He}	permeability coefficient of helium (gas)
PHBV	poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PLA	poly(lactic acid)
PLA4030D, PLA4031D,	PLA (98% L-lactide) from NatureWorks LLC
PLA4032D	
PLA4040D	PLA (94% L-lactide) from NatureWorks LLC
PLA5200D	PLA (96% L-lactide) from NatureWorks LLC (Not in
	use according to NatureWorks LLC homepage)
PLLA	PLA with isotactic sequences of L-lactide
РММА	poly(methyl methacrylate)
P_{N_2}	permeability coefficient of nitrogen (gas)
Po ₂	permeability coefficient of oxygen (gas)
PP	polypropylene
PS	polystyrene
PTFE	polytetrafluoroethylene
PVAL	poly(vinyl alcohol)
PVC	poly(vinyl chloride)
PVDC	poly(vinylidene chloride)
QCM	quartz crystal microbalance
QSM	quartz spring microbalance
RAF	restricted (or rigid) amorphous fraction
RH	relative humidity
RST	regular solution theory

S	solubility coefficient
Scio ₂	solubility coefficient of chlorine dioxide (gas)
S _{H2} 0	solubility coefficient of water vapor
SiOx	silicon oxide
So ₂	solubility coefficient of oxygen (gas)
TBHQ	tert-butylhydroquinone
Tc	critical temperature
ТЕМРО	2,2,6,6-tetramethylpiperidine-1-oxyl
T_g	glass transition temperature
TiO ₂	titanium dioxide
T _m	melting temperature
TMC-238	N,N',N"-tricyclohexyl-1,3,5-benzene-tricarboxylamide
TOCN	TEMPO-oxidized cellulose nanofiber
V	molecular volume
Vc	critical volume
v/v	volume per volume
WVTR	water vapor transmission rate
Xc	crystallinity degree
X _{MAF}	mobile amorphous fraction
X _{RAF}	restricted (rigid) amorphous fraction

CHAPTER 1

INTRODUCTION

1.1 Background and motivation

Public concerns about the negative effects of fossil-based plastics on the environment have resulted in an increase in the usage of biodegradable and compostable polymers as well as polymers made from renewable resources [1]. One of the major commercial biodegradable and renewable polymers is poly(lactic acid) (PLA), which can be made from corn, cassava, or sugar beet. Properties of PLA can be tailored based on the compositions of initial monomers in the production stage [2]. While PLA has suitable properties for applications in the medical, textile, agricultural, and packaging fields [3–6], its properties are affected by the service and storage environments such as temperature, humidity, and contacted substances.

PLA is known to be permeable to gases, vapors, and organic compounds. The values of its mass transfer parameters such as permeability, diffusion, and solubility coefficients have been reported in academic and industrial literature. However, compared to the number of the research reporting other PLA properties, literature on PLA mass transfer properties is scarce and the reported values and units are inconsistent [7]. Furthermore, a relatively new concept of the three-phase model in semicrystalline polymer that separates the amorphous phase into a rigid amorphous fraction and a mobile amorphous fraction has been proven to be applicable to PLA [8–11]. The majority of the reported PLA properties are based on the two phases, namely,

the crystalline and amorphous phases. The three-phase model has barely been considered when interpreting PLA properties.

Besides mass transfer properties of gases and vapors in PLA, there are possible interactions of PLA with solvents and aqueous solutions, which are important to consider; for example, when PLA is used in applications such as medical implant in the human body or packaging for a liquid medicine or food. In an implant, PLA is required to dissolve and eventually degrade within the body in a timely manner. On the contrary, when a PLA container is in contact with a liquid medicine or food, dissolution and degradation of PLA is considered a grave failure and possible health hazard.

A number of articles reported properties of PLA "after" being immersed in solvents and solutions; however, a limited number of articles reported changes in properties of PLA "during" the immersion (i.e., *in-situ*) [12]. While the changes after immersion may be used for prediction of interactions during immersion, the *in-situ* properties may lead to valuable insight of what is going on between PLA and the solvents and solutions in contact.

With these gaps in knowledge for PLA barrier properties, there is at least a need to reassess the mass transfer of PLA and evaluate the *in-situ* changes in PLA properties during immersion in solvents and solutions.

1.2 Overall goal and objectives

The overall goal of this dissertation is to provide a critical and systematic review of mass transfer of PLA as well as to evaluate the *in-situ* changes in PLA properties when in

contact with solvents and aqueous solutions. To achieve this goal, this dissertation aims to address two specific objectives, which are:

<u>Objective 1</u>: To provide a comprehensive, systematic, and critical review of the mass transfer of gases, vapors, and organic compounds in PLA.

<u>Objective 2</u>: To gain an understanding of the *in-situ* changes in thermo-mechanical properties of PLA when in contact with alcohol solutions.

1.3 Dissertation overview

This dissertation is organized as follows. The current chapter (Chapter 1) gives a general idea of the motivation and importance of this study including the overall goal and the specific objectives. Chapter 2 is a version of a published article that provides a comprehensive, systematic, and critical review of the mass transfer properties of PLA, which covers mass transfer background, mass transfer of gases, water vapors, and organic vapors and migration of chemical compounds in PLA, as well as comparisons of PLA barrier properties with other commercial polymers. Chapter 3 investigates the *insitu* thermo-mechanical properties of PLA during immersion in selected alcohol solutions and evaluates the relationships between the solvent molecules and the changes in the properties of PLA during immersion compared to properties before immersion. Finally, Chapter 4 summarizes the work in this dissertation with overall conclusion and recommendations for future work.

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water-ethanol solutions. Polymer (Guildf) 2016;99:315-23.

CHAPTER 2

POLY(LACTIC ACID) MASS TRANSFER PROPERTIES

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2.1 Abstract

Poly(lactic acid) (PLA), a biodegradable and compostable polymer, is gaining market acceptance and has been extensively investigated. The versatility of PLA has led to its broad and different applications in medical, agriculture, and food packaging fields. Similar to other polymers, PLA is permeable to gases, vapors and organic compounds. Thus, the mass transfer properties of PLA can influence its suitability for end-use applications. Here, we present a comprehensive, systematic, and critical review of more than 300 papers published since 1990 reporting the mass transfer properties of PLA, which include permeability, diffusion and solubility to gases, water vapor and organic vapors, along with migration of chemical compounds from PLA. Overall, PLA provides moderate barrier to gases, water vapor, and organic compounds. Barrier enhancement can be achieved through modifications such as blending with other polymers and formation of composite structures. Most of the mass transfer parameters reported in the literature are based on two-phase mobile amorphous and crystalline fractions, omitting the role of the restricted amorphous fraction, which can lead to unclear comprehension of PLA barrier properties as well as what affects those properties. Additional research is needed to address this shortcoming. This review provides an in-depth analysis of PLA mass transfer and a foundation for future research and commercial development.

2.2 Nomenclature

AP	amylopectin
ATBC	acetyl tributyl citrate
aw	water activity
BHA	butylated hydroxyanisole
BHT	butylated hydroxytoluene
Biophan	PLA from Treofan
C30B	Cloisite® 30B
CA-PBSA	crotonic acid functionalized poly(lactic acid) coupling
	poly(butylene succinate-co-adipate)
CF	crystalline fraction
D	diffusion coefficient
D _{CIO2}	diffusion coefficient of chlorine dioxide (gas)
D _{CO2}	diffusion coefficient of carbon dioxide (gas)
<i>D</i> _{H2} 0	diffusion coefficient of water vapor
Do ₂	diffusion coefficient of oxygen (gas)
DS	degree of swelling
E _D	activation energy of diffusion
E _{D,CO2}	activation energy of diffusion of carbon dioxide (gas)
<i>E</i> _{<i>D</i>,02}	activation energy of diffusion of oxygen (gas)
E _P	activation energy of permeation
E _{P,CH4}	activation energy of permeation of methane (gas)

E _{P,CIO2}	activation energy of permeation of chlorine dioxide
	(gas)
E _{P,CO2}	activation energy of permeation of carbon dioxide
	(gas)
E _{P,H2}	activation energy of permeation of hydrogen (gas)
E _{P,H2} 0	activation energy of permeation of water vapor
E _{P,N2}	activation energy of permeation of nitrogen (gas)
E _{P,O2}	activation energy of permeation of oxygen (gas)
EVLON	PLA film from BI-AX International Inc.
EVOH	ethylene vinyl alcohol
FTIR-ATR	Fourier transform infrared spectroscopy-attenuated
	total reflection
FV	free volume
HDPE	high density polyethylene
ΔH_{C}	heat of condensation
ΔH_M	heat of mixing
ΔHs	heat of sorption
IGC	inverse gas chromatography
K _{ρ,f}	partition coefficient of solute between polymer p and
	liquid f
LA	lactic acid
LDH	layered double hydroxide
LDPE	low density polyethylene

MAF	mobile amorphous fraction
MMT	montmorillonite
Mn	number-average molecular weight
Mw	weight-average molecular weight
MSB	magnetic suspension balance
NS	nanosilica
o-LA	lactic acid oligomer
OPLA	oriented poly(lactic acid)
OMMT	organically-modified montmorillonite
Р	permeability coefficient
PAN	polyacrylonitrile
PBSA	poly(butylene succinate-co-adipate)
PC	polycarbonate
P _{CH4}	permeability coefficient of methane (gas)
PCL	polycaprolactone
P _{CIO2}	permeability coefficient of chlorine dioxide (gas)
P _{CO2}	permeability coefficient of carbon dioxide (gas)
PDLA	PLA with isotactic sequences of D-lactide
PDLLA	PLA formed by meso-lactide (D,L) or a mixture of L-
	and D-lactides, or PLA polymerized from a racemic
	mixture (50:50) of L- and D-lactides
PE	polyethylene
PEG	poly(ethylene glycol)

PEN	poly(ethylene naphthalate)
PET	poly(ethylene terephthalate)
PG	propyl gallate
P _{H2}	permeability coefficient of hydrogen (gas)
<i>P</i> _{<i>H</i>₂0}	permeability coefficient of water vapor
P _{He}	permeability coefficient of helium (gas)
PHBV	poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
PLA	poly(lactic acid)
PLA4030D, PLA4031D,	PLA (98% L-lactide) from NatureWorks LLC
PLA4032D	
PLA4040D	PLA (94% L-lactide) from NatureWorks LLC
PLA5200D	PLA (96% L-lactide) from NatureWorks LLC (Not in
	use according to NatureWorks LLC homepage)
PLLA	PLA with isotactic sequences of L-lactide
PMMA	poly(methyl methacrylate)
P_{N_2}	permeability coefficient of nitrogen (gas)
Po ₂	permeability coefficient of oxygen (gas)
PP	polypropylene
PS	polystyrene
PTFE	polytetrafluoroethylene
PVAL	poly(vinyl alcohol)
PVC	poly(vinyl chloride)
PVDC	poly(vinylidene chloride)

QCM	quartz crystal microbalance
QSM	quartz spring microbalance
RAF	restricted (or rigid) amorphous fraction
RH	relative humidity
RST	regular solution theory
S	solubility coefficient
Scio2	solubility coefficient of chlorine dioxide (gas)
S _{H2} 0	solubility coefficient of water vapor
SiOx	silicon oxide
So ₂	solubility coefficient of oxygen (gas)
TBHQ	tert-butylhydroquinone
Tc	critical temperature
ТЕМРО	2,2,6,6-tetramethylpiperidine-1-oxyl
T_g	glass transition temperature
TiO ₂	titanium dioxide
T _m	melting temperature
TMC-238	N,N',N"-tricyclohexyl-1,3,5-benzene-tricarboxylamide
TOCN	TEMPO-oxidized cellulose nanofiber
V	molecular volume
Vc	critical volume
WVTR	water vapor transmission rate
X _c	crystallinity degree

2.3 Introduction

Mass transfer properties play a crucial role in the research, development, and applications of polymers. Low molecular weight gases, vapors and organic compounds can absorb into and permeate through a polymer matrix. Whether it is determining the pollutant filtration capacity of a plastic membrane [1,2] or predicting the shelf life of pharmaceutical and food products [3–6], polymer mass transfer parameters are critical to know. Nevertheless, systematic reviews of the mass transfer properties of most polymers are not readily available. For relatively new polymers such as poly(lactic acid) (PLA) - a biodegradable and bio-based polymer used for medical, agricultural and packaging applications [7,8] - data on its mass transfer properties are either scarce or widely dispersed in the technical and commercial literature. Thus, the goal of this paper is to provide a comprehensive, systematic and critical review of the mass transfer of gases, vapors and organic compounds in PLA.

PLA is by far the most researched commercial biodegradable and compostable polymer [9]. It is derived from renewable resources such as corn, cassava, and sugar beets and can be commercially produced from the condensation polymerization of lactic acid (LA) or ring-opening polymerization through lactide [7–10]. NatureWorks LLC is currently the primary producer of PLA while other companies, including LA manufacturers, are also diversifying into PLA mass production [11]. PLA, like any other polymer, is permeable to gases, vapors and organic compounds, which may impact its end-use performance. From an intrinsic factor standpoint, PLA barrier properties are affected by the enantiomer compositions of LA (i.e., L-LA and D-LA) or lactide (i.e., L-lactide and D-lactide). Different configurations of LA or lactide can result in PLA with

different crystallinity and thermal properties [12–16]. On the other hand, temperature is an extrinsic factor that affects the mass transfer properties of PLA. The increase in temperature can enhance the diffusion of gases and vapors, resulting in glass-to-rubber transition, plasticization, and deterioration of a polymer. For measuring and modeling the mass transfer parameters (i.e., permeability (P), diffusion (D) and solubility (S) coefficients) of PLA, its transition temperatures, as well as the test temperatures, must be considered [17–20]. Relative humidity (RH) is another extrinsic factor that can affect the barrier properties of PLA. Exposing PLA to high RH can plasticize the polymer, resulting in non-Fickian mass transfer phenomena [21]. While PLA may have advantages over other polymers because of its biodegradability and origin from renewable resources, it also has significant disadvantages such as brittleness, poor thermal stability, low toughness, and low elongation at break [13,22]. PLA modifications, such as blending with other polymers, incorporation of additives, formation of composites and nanocomposites, may impact its mass transfer properties in different ways [22-59]. So, a comprehensive understanding of the factors affecting PLA mass transfer properties is critical.

Research activities on PLA have significantly increased over the past few decades. Figure 2-1 shows the number of peer-reviewed publications on PLA and PLA mass transfer properties published since 1990. While the number of publications on PLA has increased exponentially in areas such as material [8,9,13,60], optical [61], thermal [57,62] and mechanical [62–65] properties, as well as its end of life [9], only a small number of the contributions are related to mass transfer. Thus, there is a need for a review of PLA barrier properties and the current data gaps.


Figure 2-1 Peer-reviewed publications on PLA^a and PLA barrier properties^b between 1990 and 2016. (^a from Web of Science[®] Core Collection search results with keywords "PLA", "poly(lactic acid)", "polylactic acid", "polylactide" and ^b from Web of Science[®] search results with keywords "PLA", "poly(lactic acid)", "polylactic acid", "polylactide" AND "mass transport", "mass transfer", "permeation", "permeability", "barrier properties", "solubility", "diffusion", "diffusivity").

The objectives of this review are:

To provide a comprehensive, systematic and critical review of experimental data

for the mass transfer parameters (i.e., P, D, and S) of PLA to gases, vapors, and

organic compounds.

• To identify the main factors affecting PLA mass transfer properties, such as

temperature, RH, morphology, ratios of L- to D-lactide, and thermal history.

- To review the modification methods, such as blends, composites and nanocomposites of PLA, and understand their effects on PLA mass transfer properties.
- To highlight mass transfer properties that have not been adequately addressed.

2.4 A short background on mass transfer in polymers

2.4.1 Mathematical approach to evaluate mass transfer

In 1829, Thomas Graham's works [66] on gas diffusion brought to the attention of researchers the mass transfer of small molecules through membranes. Small molecules (i.e., permeants) permeate through a polymer from high to low chemical potential (μ) to maintain thermodynamic equilibrium. This difference in μ is the fundamental driving force for mass transfer through polymers [67–69]. For a permeant *i*, its chemical potential, μ_i , can be expressed in terms of its chemical activity, a_i , as:

$$\mu_i = \mu_i^0 + RT \ln a_i \tag{1}$$

where μ_i^0 is the chemical potential of the permeant *i* at a standard state, *R* is the universal gas constant, and *T* is temperature in Kelvin. At a typical standard state, the chemical activity of permeant *i* is approximately equal to its concentration, c_i [67–69]. In the gas phase, concentration can be expressed as partial pressure, p_i , following the ideal gas law as expressed in Eq. 2 where n_i is the number of the permeant molecules and *v* is volume.

$$p_i = c_i RT = \frac{n_i}{\nu} RT \tag{2}$$

For a non-ideal gas, the fugacity, f_i , can be used instead of pressure [70].

Permeation in polymers consists of three steps [71]: *(i)* sorption of the permeant into the polymer matrix on the high concentration surface; *(ii)* diffusion of the permeant through the polymer matrix along a concentration gradient towards the low concentration side; and *(iii)* desorption or evaporation of the permeant from the low concentration surface. Figure 2-2 shows a schematic of the permeation process in a homogeneous polymeric film. Deviation from a straight line during the diffusion process can occur when the permeant interacts with the polymer, i.e., when the mass transfer does not follow the Fickian behavior, as may be classified as the diffusion-relaxation model for non-Fickian [21,72,73].



Figure 2-2 Permeation of small molecules from a higher to a lower chemical potential membrane or film side.

From a mass balance standpoint, assuming that diffusion takes place only in the x-direction in a polymeric membrane, the process can be described by the relationship between the flux (F) and the concentration gradient as described by Fick's first law of

diffusion [68]:

$$F = -D\frac{dc}{dx} \tag{3}$$

where *D* is the diffusion coefficient, *c* is the concentration, *x* is the direction of movement of the permeant and dc/dx is the concentration gradient in the direction of the flow. Eq. 3 can be used when the permeant concentration does not change with time (i.e., steady state). The flux of a permeant through a polymeric film is defined as the amount of permeant passing through a surface of unit area normal to the direction of flow per unit time and can be described by Eq. 4 at steady state:

$$F = \frac{Q}{At} \tag{4}$$

where Q is the amount of permeant, A is the area, and t is time. If the permeant concentrations on both sides of the film, c_1 and c_2 , remain constant, Eq. 3 can then be integrated across the total thickness of the film (L), resulting in:

$$F = D \, \frac{(c_1 - c_2)}{L}$$
(5)

By replacing *F* using Eq. 4, *Q* can be derived as:

$$Q = D \frac{(c_1 - c_2)At}{L} \tag{6}$$

When the permeant is a gas, it is more convenient to measure the vapor pressure (p), which is at equilibrium with the polymer, rather than the actual concentration within the polymer. At sufficiently low concentration and when the permeant does not interact with the polymer, Henry's law applies [68] and c can be expressed as:

$$c = Sp \tag{7}$$

where *S* is the solubility coefficient of the permeant in the polymer.

At different temperatures, amorphous regions in a polymer exist in either the glassy or rubbery state. Below the polymer's glass transition temperature (T_g), the amorphous regions are in the glassy state where segmental movements of the polymer chains are restricted, and hence the polymer tends to be rigid. Above T_g , the polymer chains have more freedom in movement. Existing in the rubbery state, the polymer tends to be flexible. For gases and aroma compounds permeating through a glassy polymer that do not obey Henry's law, the Henry-Langmuir adsorption equation (Eq. 8) can be used. The Henry-Langmuir theory takes into consideration the sorption of the gas in the frozen free volume (FV) of the polymer matrix [74]:

$$c = Sp + \frac{C'_H bp}{1 + bp} \tag{8}$$

where C'_{H} is the saturated concentration of the gas in the FV, and *b* is the FV affinity constant or ratio of rate constant for adsorption and desorption. In the case of high permeant concentration or if the permeant interacts with the polymer, the Flory-Huggins equation (Eq. 9) can be used to estimate the permeant concentration within the FV of the polymer [75]:

$$\ln a = \ln \varphi + (1 - \varphi) + \chi (1 - \varphi)^2$$
(9)

where *a* is the chemical activity of the permeant, φ is the volume fraction of the permeant in the polymer and χ is the Flory-Huggins interaction parameter between the permeant and the polymer [76].

Assuming no interaction between the permeant and the polymer, applying Henry's law (Eq. 7) to Eq. 6 results in:

$$Q = DS \frac{(p_1 - p_2)At}{L} \tag{10}$$

which can be rearranged as:

$$P = DS = \frac{QL}{At(p_1 - p_2)} = \frac{QL}{At\Delta p}$$
(11)

where *P* is defined as the permeability coefficient of a permeant at steady state and Δp is the partial pressure gradient of the permeant, $\Delta p = p_1 - p_2$. *P* can be determined from the transmission rate data or from the *P* = *DS* relationship, where *D* and *S* are determined separately [77]. This equation is very simplistic and mostly suitable for rubbery polymers. For glassy polymers, due to their restricted polymer chain mobility, permeation phenomena may deviate from this relationship.

During the unsteady state portion of mass transfer, Fick's second law describes the process of permeation [78]:

$$\frac{dc}{dt} = \frac{d}{dx} \left(D \frac{dc}{dx} \right) \tag{12}$$

where the left side of Eq. 12 is the rate of change of permeant concentration. When there is a strong polymer-permeant interaction, D is dependent on time, position, and concentration [79]. Eq. 12 may be solved using numerical methods. However, if D is time-, position- and concentration-independent, Eq. 12 can be written as:

$$\frac{dc}{dt} = D \frac{d^2 c}{dx^2} \tag{13}$$

If the unsteady state and steady state portions of the mass transfer are included and Henry's law applies, Eq. 13 can be solved as:

$$\frac{F_t}{F_{\infty}} = \left(\frac{4}{\sqrt{\pi}}\right) \left(\sqrt{\frac{L^2}{4Dt}}\right) \sum_{n=1,3,5,\dots}^{\infty} exp\left(\frac{-n^2L^2}{4Dt}\right)$$
(14)

where F_t is the flow rate of the permeant through the film at time *t* during the unsteady state portion and F_{∞} is the flow rate at equilibrium (steady state) [80]. Based on the mass transfer profile from Eq. 14, *D* can be estimated from:

$$D = \frac{L^2}{7.199t_{0.5}} \tag{15}$$

where $t_{0.5}$ is the time when F_t/F_{∞} = 0.5. *P* can be calculated if the value of F_{∞} is known:

$$P = \frac{F_{\infty}L}{\Delta p} \tag{16}$$

2.4.2 Experimental methods to quantify mass transfer in polymers

To determine permeability of gases and vapors in a polymeric film, isostatic and quasiisostatic methods are often used [81]. In the isostatic method (also known as continuous-flow method), a film is mounted in a chamber where one side of the film is exposed to a known constant concentration of the permeant and the other side of the film is maintained at near-zero permeant concentration. On the zero-concentration side, the permeant passing through the film is being purged by an inert carrier gas to a detector for quantification. After obtaining the data of permeation rate as a function of time from an experiment, Eqs.11–16 can be applied to calculate *P* and *D*. A schematic diagram and plot of the isostatic method are shown in Figure 2-3a with the unsteady state portion of the experimental data in the shaded area of the plot. In the quasiisostatic method (also known as the lag-time or constant-volume/variable-pressure method), a film is exposed to the permeant on one side and on the other side the concentration is accumulated in general to values below 5 wt% of the concentration on the high concentration side [82]. Samples of permeant from the accumulating side are taken and quantified at certain time intervals to generate a plot of permeant quantity versus time. The x-axis intercept from the steady-state portion of the plot is the lag time, t_{θ_i} , which can be used to estimate *D*:

$$t_{\theta} = \frac{L^2}{6D} \tag{17}$$

From the slope of the linear portion of the permeation plot, i.e., when the permeation is in a steady-state, *P* can be estimated [82,83]. For both methods, the environmental conditions such as temperature and RH are kept constant throughout the experiment and should be reported together with the results. Using either of the two methods, *P* and *D* can be calculated and then *S* can be estimated from P = DS assuming that Henry's law applies. A schematic diagram and plot of the quasi-isostatic method is shown in Figure 2-3b with the unsteady state portion of the experimental data in the shaded area of the plot. The water vapor transmission rate (WVTR) cup method shown in Figure 2-3c measures the weight gain from the amount of moisture transported through a film sample and absorbed by a desiccant. A plot of moisture uptake versus time can be used to calculate WVTR and *P*. The WVTR cup method has also been used for organic vapors [84,85]. An extensive review of methods to measure permeability for gases and water vapor in polymeric films can be found elsewhere in the literature [81,86].

For vapors and aroma compounds, sorption measurements may be preferable as they have some advantages over permeability measurements. For example, leakage or pinholes in the films will not affect the results [77]. In sorption measurements, the gain or loss of weight of the film is measured as a function of time while the film is exposed to a constant concentration or vapor pressure of the permeant. Equipment such as a

McBain sorption balance, magnetic suspension balance (MSB), or quartz crystal microbalance (QCM) have often been used in sorption measurements. Schematic diagrams of the McBain sorption balance and MSB are shown in Figure 2-3d and QCM in Figure 2-3e. A McBain sorption balance, named after the scientist who invented it, is a high vacuum quartz spring adsorption apparatus. Using a quartz spring, the balance can be used for measuring vapor sorption by solid surfaces [87]. For MSB, a magnetic suspension coupling is used to separate the balance from the measuring atmosphere and allows a contact-free weighing method [88]. A QCM measures weight change by measuring the change in resonant frequency of a quartz crystal where the change of mass due to absorption at the crystal surface can be mathematically calculated from the change in frequency [89]. Using microbalance systems with low partial pressure of the solute [90] may reduce mass transfer resistance for the adsorption of the solute onto the polymer surface. However, with this approach, leakages may occur on a long-running experiment. Inverse gas chromatography (IGC) shown in Figure 2-3f has resurged as a method to quantify mass transfer parameters of organic vapors in polymers. It uses a polymer packed in the IGC column as a stationary phase and a small quantity of the test compound as a mobile phase. Identification and quantification of the compound can be achieved using its response and retention time [91]. A detailed review of these sorption methods can be found elsewhere in the literature [91,92].



Figure 2-3 Common methods to measure permeability, diffusion and solubility in polymer films. Images adapted from: a. [81], b. [81], c. [86], d. [91], e. [91,93], f. [94].

2.4.3 Short background of PLA thermal properties and crystal morphology This section summarizes the thermal properties and crystalline structures relevant to PLA barrier properties. For further detailed information about these topics, the readers are directed to specific review articles [12,95,96].

PLA is synthetized from LA or lactide. Because LA and lactide have a chiral carbon (also known as an asymmetric carbon), they exist in different enantiomers (Figure 2-4a). Different amounts of LA or lactide enantiomers can be combined to produce the final high molecular weight PLA with a basic repeating unit as shown in Figure 2-4b, which has a molar mass of 72.06 g.mol⁻¹. PLA formed by isotactic sequences of L-lactide (or L-LA) and D-lactide (or D-LA) are commonly referred to as PLLA and PDLA, respectively. However, the term PDLLA may represent PLA formed by *meso*-lactide or a mixture of L- and D-lactide (or L- and D-LA), or PLA polymerized from a racemic mixture (50:50) of L- and D-lactides (or L- and D-LA). To avoid confusion, this review will refer to PLA by its L- or D- enantiomer composition in the final product (e.g., PLA 92% L), regardless of its production or processing methods used. Depending on the combination of LA or lactide, final PLA properties can be tailored and changed [8]. Readers may refer to the original papers for details on PLA samples included in this review.



Figure 2-4 a) Chemical structures of a) L(+), D(-) lactic acid, L-lactide, D-lactide and *meso*-lactide and b) PLA repeating unit with an asterisk (*) indicating the chiral carbon atom.

In general, the T_g and melting temperature (T_m) of PLA are affected by the L- and D-lactide contents. Bigg [97] reported a reduction in T_g as the amount of D-lactide increased in (L-/D,L) random copolymers of PLA (i.e., poly(L-*co*-D,L-lactides), made from copolymerization of poly(L-lactides) with copolymers made from a random copolymer of 50% L- and 50% D-lactide). However, as shown in Figure 2-5a, when D-lactide exceeds 5%, T_g no longer changes. Feng et al. [98] recently reported a reduction in T_g with increasing amount of D-lactide when various combinations of lactide enantiomers were used as comonomers in PLA copolymers (also shown in Figure 2-5a). Similarly, a reduction in T_m was observed as the amount of D-lactide increased [60,97–101], as shown in Figure 2-5b. Furthermore, Feng et al. [98] highlighted that the differences in T_g and T_m between poly(L-*co*-D-lactides) and poly(L-*co-meso*-lactides) with the same amount of D-lactide were a result of different contributions of D-lactide and *meso*-lactide to the disruption (i.e., disorder degree) of PLA molecular chain tacticity. Saeidlou et al.

[12] conducted an extensive review of PLA crystallization and reported the variation of T_g as a function of number-average molecular weight (M_n) [60,102–104], as shown in Figure 2-6. Apparently, as M_n reaches about 100 kg.mol⁻¹, T_g remains stable regardless of the type of PLA. The effect of the ratio of L:D-lactide is also evident in Figure 2-6 that T_g tends to decrease as the ratio of D-lactide increases.



Figure 2-5 a) Glass transition (T_g) and b) melting (T_m) temperatures of PLA with various combinations of lactide enantiomers versus %D-lactide, adapted from [7,12,98]. References: a [98], b [97], c [99], d [60], e [100], f poly(L-*co*-D-lactides) [98], g poly(L-*co*-*meso*-lactides) [98], h [101]. Each dashed line is based on a linear regression of the overall data in each paper, except for T_g of poly(L-*co*-D,L-lactides) [97] that has two linear regression lines (%D-lactide = 0–5 and then %D-lactide = 5 or higher).



Figure 2-6 Glass transition temperature (T_g) versus number-average molecular weight (M_n) for PLA with different L:D-lactide ratios, adapted from [7,12]. Dashed lines are predicted lines based on the Flory-Fox equation [105]. References: ^a [102], ^b [103], ^c [104], ^d [60].

PLA exhibits four main crystal structures, namely α , β , γ , and δ (or sometimes

referred to as α ' or disordered α) [12,14,106]. Their crystal systems, chain

conformations and cell parameters are summarized in Table 2-1. Extensive reviews of

PLA crystal structures have been published [12,95,96].

	Crystal system	Helical	Cell parameters			
Crystal form		chain confor- mation	<i>a</i> , nm	<i>b</i> , nm	<i>c,</i> nm	References
α	Pseudo- orthorhombic		1.03–1.07	0.59–0.64	2.78–2.88	[61.107–112]
	Orthorhombic	10 ₃	1.05–1.07	0.60–0.61	2.87–2.88	[0.,.01 1.2]
β	Orthorhombic	31	1.03–1.04	1.77–1.82	0.90	[109,113,114]
	Trigonal		1.05	1.05	0.88	
Ŷ	Orthorhombic	3 ₁	0.99	0.62	0.88	[115]
δ (or α')	Pseudo-hexagonal	n/a	1.08	0.62	2.88	[14]
n/a: not a	wailabla					

Table 2-1 Crystal forms and systems, chain conformations and cell parameters reported for PLA.

n/a: not available

Polymer chains of PLA are longer than the thickness of the crystal lamellae, and therefore they can be entangled on different phases according to the degree of coupling. In the past, a semicrystalline polymer was believed to be composed of an amorphous phase and a crystalline phase. Michaels and Bixler [116] studied the solubility of gases in polyethylene (PE) and proposed that it was sufficient to consider PE as consisting of two phases, amorphous and crystalline, and that the crystalline phase in PE did not sorb gas molecules to a measurable extent. However, later work of Menczel and Wunderlich [117] showed that the amorphous portions in semicrystalline polymers were different from the amorphous portions in fully amorphous polymers. Later on, Wunderlich [118] examined heat capacities of semicrystalline polymers and correlated a negative contribution to heat capacity between T_g and T_m to another phase in a semicrystalline polymer called a rigid amorphous region, which exists due to a

strong coupling between the crystalline and the amorphous phases. Recently Nguyen et al. [119] demonstrated that in PLA and poly(ethylene terephthalate) (PET), the amount of crystalline fraction (X_c) and the amount of amorphous fraction (X_a) did not add up to one, which invalidated the two-phase model. In the case of PET, the deviation from the two-phase model starts at $X_c < 0.1$, but in PLA the deviation occurs at a relatively higher crystallinity ($X_c > 0.3$). Figure 2-7 shows how PLA deviates from the two-phase model as reported by a number of authors [119–121]. A dashed line represents the two-phase model, where $X_a + X_c = 1$. Deviation from the dashed line implies the presence of a third phase. The degrees of deviation vary likely due to the different crystallization methodologies applied and samples of different L-lactide contents used. Additional evidence of the deviation from the two-phase model in PLA and PET can be found in the literature [122–127].



Figure 2-7 PLA phase model determination. The dashed line represents a two-phase model with crystalline weight fraction (X_c) and amorphous weight fraction (X_a), where the sum of these two fractions equals to one. References: ^a PLA 96–97% L annealed to get semicrystalline samples [119], ^b PLA 100% L exposed to methanol after drying [121], ^c PLA 100% L exposed to ethanol after drying [121], ^d PLA 98% L (4032D) [120].

These findings contributed to the evidence for the assumption of a three-phase model in semicrystalline polymers. The proposed three phases are (1) a crystalline fraction (CF); (2) a mobile amorphous fraction (MAF); and (3) a restricted or rigid amorphous fraction (RAF). Figure 2-8 shows a possible schematic representation of these three domains where the RAFs are constrained by the adjacent CFs. Alternatively, Delpouve et al. [128] used calorimetric methods to investigate the amorphous phase dynamics in semicrystalline PLA. They proposed that besides the CF, three amorphous phases with different molecular mobilities could coexist, namely,

the RAF, the inter-spherulitic MAF and the intra-spherulitic MAF. Different models such as one with the CF surrounded by a continuum of mobility of the RAF and the MAF [129] were also proposed for other polymers.



Figure 2-8 A possible schematic representation of the crystalline fraction (CF), the restricted amorphous fraction (RAF), and the mobile amorphous fraction (MAF), adapted from [130].

So, the tentative structures that can be found in PLA films below T_g are shown in Table 2-2. In general, PLA with greater than 8% D-lactide is totally amorphous while that with less than 8% D-lactide is semicrystalline. The highest percentage of D-lactide used in commercial PLAs is approximately 12%.

Amount of D-lactide	Structure		Possible crystallinity model	References
8–12% ^a	MAF	amorphous	One phase	[7,131]
2–8%	MAF, RAF and CF	semicrystalline	Three-phase	[132]
<1%	MAF, RAF and CF	semicrystalline	Three-phase	[132]

Table 2-2 Tentative PLA crystallization model structures for PLA samples below T_{g} .

^a This applies to commercial PLA where the highest percentage of D-lactide is $\sim 12\%$.

The formation of the RAF depends of the polymer and the crystallization processes [132,133]. Del Rio et al. [134] showed that during the annealing of PLA, the MAF decreased while the RAF and the CF increased. They explained that the formation of new voids of smaller FV increased through the crystallization process due to the vitrification of the RAF chains. They also attributed the increase in FV fraction of PLA during annealing to the difference in FV void size and distribution between the RAF and the MAF, which contributed to a de-densification of the non-crystalline domain of PLA, as illustrated in Figure 2-9.



Figure 2-9 a) Crystalline (CF), restricted amorphous (RAF), and mobile amorphous (MAF) fractions of PLA samples versus annealing time at 100 °C. b) Free volume fraction increment of PLA samples versus annealing time at 100 °C. Point Q on the x-axis indicates the as-quenched sample. Figures adapted from [134].

2.4.4 Factors affecting mass transfer in polymers

As mentioned in Section 2.3, mass transfer in polymers is affected by intrinsic and extrinsic factors. The nature of the polymer such as chemical composition, polarity, stiffness of the polymer chains, bulkiness of side- and backbone-chain groups and the degree of crystallinity significantly impact the sorption and diffusion of a permeant [135]. A semicrystalline polymer can have varying degrees of crystallinity depending on processing conditions and thermal history. A higher degree of crystallinity, within the same generic class of polymer, usually affords a stronger barrier, since the permeant cannot diffuse through the crystalline domains [116,136]. It is generally accepted that for semicrystalline rubbery polymers, *D* and *S* can be expressed as:

$$D_{SC} \approx D_a (1 - X_c) \tag{18}$$

$$S_{SC} \approx S_a (1 - X_c) \tag{19}$$

where D_{sc} and S_{sc} are the *D* and *S* of a semicrystalline rubbery polymer, respectively; D_a and S_a are the *D* and *S* of the same polymer in the amorphous phase, respectively; and X_c is the degree of crystallinity of the polymer, which can be expressed in terms of mass or volume fractions of the polymer that is crystalline. Based on the relationship P = DS (Eq. 11), *P* for semicrystalline rubbery polymers [137] can be expressed as:

$$P \approx D_{SC}S_{SC} \approx D_a S_a (1 - X_c)^2 \tag{20}$$

For polymers such as PLA, PET and poly(ethylene naphthalate) (PEN), Eq. 20 may not be applicable when the mass transfer measurement is carried out below their T_g 's. The two-phase model is no longer applicable when the semicrystalline polymers are comprised of three phases (i.e., CF, RAF and MAF). Theoretically with the three-phase model, D_{sc} and S_{sc} may be expressed as:

$$D_{SC} = D_{MAF} \cdot X_{MAF} + D_{RAF} \cdot X_{RAF}$$
(21)

$$S_{SC} = S_{MAF} \cdot X_{MAF} + S_{RAF} \cdot X_{RAF}$$
(22)

where D_{MAF} , S_{MAF} and X_{MAF} are the D, S and the mass or volume fraction of the MAF, respectively; D_{RAF} , S_{RAF} and X_{RAF} are the D, S and the mass or volume fraction of the RAF, respectively.

The nature of the permeant also plays an important role in mass transfer. For a series of chemically similar permeants, an increase in the size of a permeant generally results in an increase in *S* and a decrease in *D* [138]. Likewise, the polarity of the polymer and the permeant and their affinity affect the extent to which the permeant dissolves in the polymer. As for the environmental effects, the Arrhenius relationship can be used to describe the temperature dependence of mass transport properties [136]:

$$P = P_o exp\left(-\frac{E_P}{RT}\right) \tag{23}$$

$$D = D_o exp\left(-\frac{E_D}{RT}\right) \tag{24}$$

$$S = S_o exp\left(-\frac{\Delta H_S}{RT}\right) \tag{25}$$

where P_o , D_o and S_o are the pre-exponential factors for P, D, and S, respectively. E_P is the activation energy of permeation, E_D is the activation energy of diffusion, and ΔH_S is the heat of sorption. The Arrhenius relationship is applicable both below and above T_g , but as segmental chain movements are dependent on T_g due to the change of FV [139] (see Figure 2-10), the relationship is not applicable across the glass-rubber transition [81,140]. Overall, E_P can be expressed as the sum of E_D and ΔH_S (Eq. 26). Furthermore, ΔH_S can be expressed as the sum of ΔH_C , the heat of condensation, and ΔH_M , the heat of mixing (Eq. 27):

$$E_P = E_D + \Delta H_S \tag{26}$$

$$\Delta H_S = \Delta H_C + \Delta H_M \tag{27}$$

Additional factors such as moisture in the environment can also play a role in the mass transfer. For example, moisture can swell the polymer and/or act as a plasticizer, resulting in an increased flexibility in segmental chain movement of the polymer and leading to an increase in *D*. On the other hand, water molecules can cluster on the polymer surface and impede sorption of the permeant [141].



Figure 2-10 Specific volume diagram of a polymer as a function of temperature (T), adapted from [142]. An increase in free volume is observed above the glass transition temperature (T_g).

2.5 Mass transfer of gases in PLA films

The *P*, *D*, and *S* of pure gases such as O_2 , CO_2 , N_2 , and CH₄ in PLA films are discussed in this section. We begin by presenting an overall summary of PLA mass transfer properties, followed by the specific details of *P*, *D*, and *S* for a set of gases and vapors. Various factors affecting mass transfer properties are discussed in the respective subsections. The effects of PLA modifications on mass transfer properties are discussed, followed by highlighting data gaps and recommendations for future research. Since *P*, *D*, and *S* for O_2 have been extensively reported, we provide a dedicated section on mass transfer of this specific permanent gas in Section 2.6. An arbitrary T_g of 58 °C is used throughout the review when discussing temperature ranges below and above T_g . To compare results from different sources, reported *P*, *D*, and *S* values were converted to the same S.I. units, i.e., kg.m.m⁻².s⁻¹.Pa⁻¹ for *P*, m².s⁻¹ for *D*, and kg.m⁻³.Pa⁻¹ for *S*. Measurements with units that could not be converted into these specific units are discussed separately or were excluded.

In summary, under dry conditions, the *P* values follow the Arrhenius relationship with temperature, with a discontinuous trend below and above T_g . However, limited availability and large dispersion of data for *D* and *S* values made it difficult to establish definite trends for the effects of temperature. The *P* values show an increasing trend as the molecular weights of the gases increase, but a decreasing trend as the kinetic diameters of the gases increase. The *D* values have a decreasing trend as the critical volumes of the gases increase, while the *S* values have an increasing trend as the critical temperatures of the gases increase.

2.5.1 Permeability

An Arrhenius plot of *P* (based on Eq. 23) of selected pure gases in neat PLA films at 0% RH (i.e., dry conditions) is shown in Figure 2-11. Overall *P* for O₂, CO₂, N₂, H₂, He and CH₄ gases are lower than 7×10^{-17} kg.m.m⁻².s⁻¹.Pa⁻¹ below *T_g*. Above *T_g*, the overall *P* of these gases are lower than 3×10^{-16} kg.m.m⁻².s⁻¹.Pa⁻¹. The magnitude of *P* of pure gases at 0% RH observed in Figure 2-11 follows this trend: CO₂ > He > H₂ > O₂ > N₂ > CH₄ below *T_g*, with the trend of CO₂ > O₂ > H₂ > N₂ above *T_g*. Arrhenius relationships were observed for all the gases and the changes in slopes of the linear regression lines below and above *T_g* implies discontinuous barrier properties of PLA across the *T_g* range.

Compared to our reported trend in *P* of pure gases, Sawada et al. [143] and Komatsuka and Nagai [144] reported the trend being H₂ > CO₂ > O₂ > N₂ > CH₄, with unit of *P* in cm³(STP).cm.cm⁻².s⁻¹.cmHg⁻¹. After converting their values to kg.m.m⁻².s⁻¹.Pa⁻¹, which expressed *P* in mass instead of volume, a similar trend in all three studies was observed. Lehermeier et al. [145] reported *P* values of O₂, CO₂, N₂ and CH₄ that are 1–2 orders of magnitude higher than the average reported *P* values in this review. They initially attributed this to the processing method. However, the same group of authors reevaluated permeability of O₂, CO₂ and N₂ and reported new values and determined that the previous measurements were out of range due to the measurement method and possible presence of pinholes in very thin films [83]. Therefore, values from Lehermeier et al. [145] are not included in the plot. Furthermore, *P* values of ClO₂ (*P*_{ClO₂}) at 50% RH and different temperatures are available [146] (data not shown) and the values are higher than those of the gases discussed in Figure 2-11. (P_{ClO_2} will be discussed further in the next section). The test conditions for the measurements of *P* values of these gases and the corresponding references are summarized in Table 2-3.



Figure 2-11 Arrhenius plot of permeability coefficients (*P*) for O₂, CO₂, N₂, H₂, He and CH₄ at dry conditions. Data references: O₂ = [147], \triangleleft [144], \triangledown [133], * [58,59,83,143, 148–188]. CO₂ \circ [63], \Box [144], \Diamond [172], \triangle [58,83,143,156,173,176,177,184–186,189]. N₂ \bullet [144], \blacksquare [143], \blacklozenge [83,156,167,179,190]. H₂ x [143,144]. He \triangleright [133,155,161,165,191]. CH₄ + [143]. The vertical dash-dotted line is an arbitrary *T_g* of 58 °C and the dashed lines are from linear regressions of reported experimental data below and above *T_g*.

Gas	Temperature, °C	RH, %	References
O ₂	5–85	0–100	[58,59,63,83,143–145,147–188,192–224]
CO ₂	7–85	0–75	[58,63,83,143,144,156,172,173,176,177,
			184–186,189,192,200,204,216]
N ₂	22–85	0–50	[83,143,144,156,167,179,190,216]
H ₂	35–85	0	[143,144]
CH ₄	0–50	0	[143,145]
He	20–35	0	[133,143,155,161,163,165,168,191]
CIO ₂	23–40	50	[146]

Table 2-3 Test conditions (temperature and RH) for permeability coefficient (P) measurements of neat PLA films for selected pure gases from the literature data used in this review.

As shown in Table 2-3, it is apparent that for most gases, P values were measured only at some test temperatures and RH ranges. This could be due to difficulties in the experiment setups or the limitations of the detector to detect a small amount of the permeated gas. Nevertheless, these missing experimental conditions should be explored to better understand the factors affecting P of gases in PLA.

A plot of *P* versus molecular weight (M_w) of gases, with the y-axis on a logarithmic scale, is shown in Figure 2-12a. To reduce environmental effects such as from temperature and moisture, data were selected from measurements with similar test conditions, 0% RH and 20–35 °C, except for P_{ClO_2} which was measured at 50% RH. From Figure 2-12a, low molecular weight gases such as He and H₂ have unusually high permeability compared to other gases that display an increasing trend in *P* as their

molecular weight increases. Plotting average *P* against kinetic diameters (Figure 2-12b) shows unusually low P for He and H₂, and a linear decreasing trend as kinetic diameters increase for other gases. CIO₂ is not included in Figure 2-12b because the kinetic diameter for CIO₂ is not available. Some pioneer studies [225,226] reported decreasing diffusivities as the molecular weights of gases and vapors increased. For He and H₂, their high P values in P versus M_w plot are indicative of a dominant diffusion effect due to higher diffusivity of the small gas molecules. On the other hand, their low P values in P versus kinetic diameter can be attributed to their low solubility in the polymer. FV void sizes in PLA are reported to be 86.5 Å³ in a 60-min annealed sample and 98.7 Å³ in an as-quenched sample [134]. Accordingly, the diameter of the FV voids in PLA would range from 5.5 to 5.7 Å. He and H₂, with kinetic diameters of 2.6 and 2.9 Å, respectively, should go through the FV voids more easily than other gases with larger kinetic diameters. However, CO₂, with a kinetic diameter of 3.3 Å, has higher *P* than He and H₂ despite its larger size. This may imply dominant solubility effect as the kinetic diameters of gases increase. In low barrier polymers with large free volume, such as poly(trimethylsilyl)propyne, the sizes of these gases (He, H₂, CO₂, O₂, N₂, CH₄) have been reported to directly affect P values [227]. However, the relationship of P and the sizes or molecular weights of the gases should not be concluded without the knowledge of D and S.



Figure 2-12 Plot of average permeability coefficient (*P*) values, with standard error bars, as a function of a) molecular weights (M_w) and b) kinetic diameters of different gases for neat PLA at 20–35 °C and 0% RH [58,59,63,83,133,137,143,144,147,149–191,211], except for P_{CIO2} which were measured at 50% RH [146]. Each dashed line is a linear trend line, which excludes H₂ and He. The coefficients of determination (r^2) for the linear trend lines are a) 0.9261 and b) 0.9730.

<u>Effect of temperature</u>: Table 2-4 shows E_P , E_D , and ΔH_S values for selected gases in PLA as reported in individual publications, as well as the values estimated from linear regressions of the data from Figure 2-11. (O_2 will be discussed separately in Section 2.6). Several authors [63,83,144,172] examined P_{CO2} of PLA films at different temperature ranges and observed an Arrhenius relationship. Auras et al. [63] reported activation energy of permeation of CO2 (EP,CO2) for PLA films with 98% L-lactide and PLA films with 94% L-lactide as 15.6 and 19.4 kJ.mol⁻¹, respectively. Bao et al. [83] reported E_{P,CO_2} for PLA films with 98.7%, 80%, and 50% L-lactide as 18.5, 17.8, and 14.3 kJ.mol⁻¹, respectively. Komatsuka and Nagai [144] measured P_{CO_2} at a temperature range below and above T_g (35–85 °C) and did not find any evidence of discontinuity across the T_g range for films from 96% L-lactide and blends of 96% Llactide and 88% L-lactide. They reported E_{P,CO_2} as 48.9 kJ.mol⁻¹ for 96% L-lactide and 41.5 kJ.mol⁻¹ for the blends. E_{P,CO_2} estimated from data reported by Sansone et al. [172] for neat PLA and neat PLA after a high-pressure pasteurization process between 33 and 48 °C were 27.9 and 21.0 kJ.mol⁻¹, respectively. Linear regressions of Arrhenius relationship for P_{CO_2} data collected in this review, as shown in Figure 2-11, resulted in E_{P,CO_2} of 21.6±7.0 kJ.mol⁻¹ below T_g and 47.9±13.5 kJ.mol⁻¹ above T_g .

P values of N₂ (P_{N_2}) also show an Arrhenius relationship [144,190]. Komatsuka and Nagai [144] reported the activation energy of permeation of N₂ (E_{P,N_2}) at dry conditions between 35 and 58 °C for PLA 96% L-lactide and blends of 96% L-lactide and 88% L-lactide as 59.0 and 52.8 kJ.mol⁻¹, respectively. E_{P,N_2} estimated from P_{N_2} data from Sato et al. [190] for PLA 4032D from 25 to 45°C is 28.4 kJ.mol⁻¹. E_{P,N_2} from data in this review are 31.5±11.6 kJ.mol⁻¹ below T_g and 57.0±12.7 kJ.mol⁻¹ above T_g .

P values of H₂ (*P*_{H₂}) were also reported at dry conditions by Komatsuka and Nagai [144] with activation energy of permeation of H₂ (*E*_{*P*,H₂}) between 35 and 58 °C for PLA 96% L-lactide and blends of 96% L-lactide and 88% L-lactide of 33.5 and 27.0 kJ.mol⁻¹, respectively. From data in this review, *E*_{*P*,H₂} values are 30.7±8.5 and 27.3±10.5 kJ.mol⁻¹ at temperatures below and above *T*_g, respectively.

Lehermeier et al. [145] studied the temperature dependence of P_{CH_4} in 100% linear PLA with L:D ratio of 96:4 and obtained activation energy of permeation of CH₄ (E_{P,CH_4}) of 13.0 kJ.mol⁻¹ at a temperature range from 0 to 50 °C, where *P* increased from 2.73×10⁻¹⁸ to 6.38×10⁻¹⁸ kg.m.m⁻².s⁻¹.Pa⁻¹. Netramai et al. [146] reported activation energy of permeation of ClO₂ (E_{P,ClO_2}) at 50% RH as 129.03 kJ.mol⁻¹, where P_{ClO_2} increased from 5.40×10⁻¹⁷ kg.m.m⁻².s⁻¹.Pa⁻¹ at 23 °C to 9.44×10⁻¹⁶ kg.m.m⁻².s⁻¹.Pa⁻¹, which is 17 times higher, at 40 °C. To date, there is no research on temperature dependence of PLA barrier properties for He.

The reported E_P values vary and do not exhibit the same trends, which could be due to different PLA sources, processing methods or treatments. However, knowing an approximate value of E_P will help to determine an acceptable temperature range for PLA applications. Furthermore, even though Komatsuka and Nagai [144] reported no transition at the T_g region, plotting their data together with data from other authors may suggest otherwise. For example, Figure 2-11 shows noticeable transitions for *P* of gases below and above T_g , which is to be expected. Higher values of E_P for CO₂, O₂, and N₂ above T_g indicates that at higher temperatures the thermal effect on permeability is higher, so the change in permeation values is higher. However, the same trend was not found for H₂. E_P values for He have not been reported in the literature although similar behavior would be expected.

Gas	Temperature	PLA	E _{P,}	E _{D,}	ΔH _{S,}	Ref.
	range, °C		kJ.mol ^{−1}	kJ.mol ⁻¹	kJ.mol ^{−1}	
CO ₂	25–45	98% L (4030Dª)	15.6	n/a	n/a	[63]
	25–45	94% ∟ (4040Dª)	19.4	n/a	n/a	[63]
	23–45	98.7% ∟́	18.5	36.3	-18.4	[83]
	23–45	80% L	17.8	32.2	-13.9	[83]
	23–45	50% L	14.3	34.8	-25.4	[83]
	35–85	96% L	48.9	n/a	n/a	[144]
	35–85	96%:88% ∟ blends	41.5	n/a	n/a	[144]
	33–48	Biophan⁵	27.9	n/a	n/a	[172]
	33–48	Biophan ^b after high-pressure	21.0	n/a	n/a	[172]
	20–40	80% L	n/a	n/a	-21.88	[193]
	10–40	98% L	n/a	n/a	-23.14	[228]
	30–50	80% L	n/a	n/a	-22.22	[229]
	30–50	98% L	n/a	n/a	-21.58	[229]
	5–58	(various)	21.6±7.0	4.6±13.4	−22.4±1.4	This review
	59–90	(various)	47.9±13.5	n/a	n/a	This review
N_2	35–85	96% L	59.0	n/a	n/a	[144]
	35–85	96%:88% ∟ blends	52.8	n/a	n/a	[144]
	25–45	98% ∟ (4032Dª)	28.4	n/a	n/a	[190]
	23–45	98.7% ∟́	34.6	59.3	-25.0	[83]
	23–45	80% L	40.9	n/a	n/a	[83]
	23–45	50% L	35.0	n/a	n/a	[83]
	5–58	(various)	31.5±11.6	n/a	n/a	This review
	59–90	(various)	57.0±12.7	n/a	n/a	This review
H_2	35–85	96% L	33.5	n/a	n/a	[144]
	35–85	96%:88% ∟ blends	27.0	n/a	n/a	[144]
	5–58	(various)	30.7±8.5	n/a	n/a	This review
	59–90	(various)	27.3±10.5	n/a	n/a	This review
CH_4	0–50	96% L	13.0	n/a	n/a	[145]
CIO ₂	23–40	EVLON ^c	129.0	n/a	n/a	[146]

Table 2-4 Activation energy for permeation (E_P), activation energy of diffusion (E_D), and heat of sorption (ΔH_S) for selected gases at 0% RH, except for ClO₂ at 50% RH.

n/a: not available, ^a PLA from NatureWorks LLC, ^b PLA from Treofan, Germany, ^c PLA from BI-AX International Inc., Canada.

<u>Effect of relative humidity:</u> Other than the information provided for *P* values of O_2 (P_{O_2}) as a function of RH, none of the authors reported the effect of RH on *P* of other pure gases. So, it is not possible to determine the effect of RH on *P* of pure gases from the available data. For N₂, Samuel et al. [216] reported P_{N_2} of PLA 4032D at 50% RH and 22 °C of 7.23×10⁻²⁴ kg.m.m⁻².s⁻¹.Pa⁻¹. However, compared with P_{N_2} of the same type of PLA tested by other authors [167,190] at dry conditions and similar temperature (25 °C), which averages 3.22×10^{-19} kg.m.m⁻².s⁻¹.Pa⁻¹, PLA appears to have much better barrier to N₂ at 50% RH than at dry conditions, which does not seem possible. This could be attributed to different methods of measurement and sample preparation. A controlled experiment, which varies only the RH where other factors are kept constant, is required to verify the effect of RH on *P* of gases.

Effect of crystallinity and L:D ratio: Sawada et al. [143] reported that P_{H_2} , P_{CO_2} , P_{O_2} , P_{N_2} , and P_{CH_4} for PLA increased with crystallinity from 0 to 9% X_c and then decreased from 9 to 40% X_c at 35 °C and 0% RH for PLA with 96% L. Ortenzi et al. [186] reported a slight decrease in P_{CO_2} as X_c increased from 1.7% to 10.3% at 23 °C, 0% RH. Komatsuka and Nagai [144] studied P_{CO_2} at 35–85 °C and 0% RH and reported no significant effect of X_c on P_{CO_2} between 35 and 55 °C, but an increase in P_{CO_2} as X_c increased from 7.4 to 24.8% between 65 and 85 °C. Colomines et al. [155] observed no effect of X_c on P_{He} at 23 °C and 0% RH for PLA with 2–39% X_c . On the other hand, Guinault et al. [161] reported a decrease in P_{He} at 23 °C and 0% RH for PLA of 98% L-lactide with 2–40% X_c , but an increase in P_{He} from 2 to 40% X_c and then a decrease from 40 to 60% X_c at the same test conditions for PLA with 99% L-lactide. Courgneau et al. [168] reported decreasing P_{He} at 23 °C and 40–60% RH for PLA with 3–43% X_c . Guinault et al. [133] tested PLA with different degrees of crystallinity at 23 °C and 0% RH and found no effect of crystallinity on P_{He} at low crystallinity (2–40% X_c for PLA with 99% L-lactide and 1–20% X_c for PLA with 96% L-lactide). However, they reported decreasing P_{He} at higher % X_c (50–63% X_c for PLA with 99% L-lactide and 30–44% X_c for PLA with 96% L-lactide). These findings on the effect of crystallinity are summarized in Table 2-5.
PLA	Gas(es)	Change in P as X_c increased	T, °C	RH, %	<i>X</i> _c , %	Ref.
96% L	H ₂ , CO ₂ , O ₂ , N ₂ , CH ₄	increased	35	0	0–9	[143]
96% L	$H_2, CO_2, O_2, N_2, CH_4$	decreased	35	0	9–40	[143]
n/a	CO ₂	decreased	23	0	2–10	[186]
96% L	CO ₂	no change	35–55	0	7–25	[144]
96% L	CO ₂	increased	65–85	0	7–25	[144]
n/a	Не	no change	23	0	2–39	[155]
98% L	Не	decreased	23	0	2–40	[161]
99% L	Не	increased	23	0	2–40	[161]
99% L	Не	decreased	23	0	40–60	[161]
92% L	Не	decreased	23	40–60	3–43	[168]
96% L	Не	no change	23	0	1–20	[133]
99% L	Не	no change	23	0	2–40	[133]
96% L	Не	decreased	23	0	30–44	[133]
99% L	Не	decreased	23	0	50–63	[133]

Table 2-5 A summary	of changes in permea	bility coefficients (P)	of gases in PLA as
degree of crystallinity	(X_c) increases.		

n/a: not available

As for the effect of L:D ratio, Auras et al. [63] and Bao et al. [83] reported P_{CO_2} at 30 °C and 0% RH for PLA with different percentages of L-lactide. Bao et al. [83] show a decrease in P_{CO_2} when L-lactide increases from 50 to 80% and an increase in P_{CO_2} as Llactide increases from 80 to 98.7%. Similarly, Auras et al. [63] report an increase in P_{CO_2} as L-lactide increases from 94% to 98%. These trends also apply to the effect of crystallinity since for these samples, % X_c increases as L-lactide increases with exceptions for PLA 50% L-lactide and 80% L-lactide as both of them have 0% X_c . Auras et al. [63] reported a slight increase in P_{CO_2} at 25 °C, 0% RH as L-lactide goes up from 94 to 98% (X_c goes up from 25 to 40%). These unusual changes could be explained by the three-phase model discussed in more detail in the section on mass transfer of O₂ (Section 2.6).

2.5.2 Diffusion

Figure 2-13 shows an Arrhenius plot of *D* (based on Eq. 24) for O₂, CO₂, CH₄, and N₂ in PLA at dry conditions. Overall, *D* of these gases at 0% RH are less than 1×10^{-11} m².s⁻¹ below *T_g*. To date, there are no reports on *D* of these gases above *T_g*. A large dispersion of the data may be due to different methods of testing and film processing as well as film defects. Plotting the average *D* values of gases against the critical volumes (*V_c*) of the gases (Figure 2-14) shows that for gases that do not interact with PLA, the size of the permeant plays an important role in the diffusion process, with smaller permeants diffusing faster as expected.

While the linear regressions (shown as dashed lines in Figure 2-13) suggest an increase in *D* values of O_2 (D_{O_2}) as temperature goes up, individual data such as those reported by Auras et al. [148] did not show the same trend. For the other gases, i.e., N₂ and CH₄, the test temperatures at 0% RH were not sufficient to estimate an Arrhenius relationship. Figure 2-14 shows a plot of average *D* values at similar test conditions (0% RH and 20–35 °C) from our review versus V_c of the gases. The y-axis (*D* values) is in a logarithmic scale. A trend of decreasing *D* as V_c increases is observed, which agrees

with results reported by Sawada et al. [143]. This trend follows an assumption that a permeant with a larger size generally has a lower *D*. Semi-empirical approaches to predict *D* values of chemicals in and through polymers using different scaling laws have been summarized by Fang and Vitrac [17]. *D* value of CIO_2 (D_{CIO_2}) was reported as 2.86±0.18×10⁻¹⁴ m².s⁻¹ at 23 °C and 50% RH [146], which is lower than most of the reported *D* values for other gases, except some of those for O₂. Since the *V_c* value of CIO₂ is not available, D_{CIO_2} is not plotted in Figure 2-14.



Figure 2-13 Arrhenius plot of diffusion coefficients (*D*) for O₂, CO₂, N₂, and CH₄. Data references: O₂ \triangleright [148], \triangleleft [83], \bigtriangledown [143], * [133], \blacksquare [163,165,166,168,169,176,180,205]. CO₂ \triangle [83,143,176,205]. N₂ \diamond [83,143,205]. CH₄ + [143]. Each dashed line represents a least squares linear regression of each gas from the reported experimental data.



Figure 2-14 Plot of average diffusion coefficient (*D*) values, with standard error bars, as a function of critical volume (V_c) of different gases for neat PLA at 20–35 °C and 0% RH [83,133,143,148,163,165,166,168,169,176,180,205]. The dashed line is a linear trend line for ln(*D*) versus V_c . The coefficient of determination (r^2) is 0.8286.

<u>Effect of temperature</u>: The trend line for CO₂ from the Arrhenius relationship (Eq. 24) in Figure 2-13 yields the activation energy of diffusion of CO₂ (E_{D,CO_2}) of 4.6±13.4 kJ.mol⁻¹ which contradicts the higher E_{D,CO_2} of 32–36 kJ.mol⁻¹ reported by Bao et al. [83] (as shown in Table 2-4). However, *D* values of CO₂ (D_{CO_2}) at each temperature were reported by different researchers [83,143,205] using different sources of PLA films resulted in a large variability in the estimated E_{D,CO_2} value. As a result, the estimated E_{D,CO_2} in this review may not represent the expected value of E_{D,CO_2} . Studies to determine the effect of temperature on D_{CO_2} by controlling other intrinsic and extrinsic factors are suggested.

<u>Effect of relative humidity</u>: The effect of RH on *D* of gases has not been explored, indicating large data gaps in the measurements of *D*.

<u>Effect of crystallinity and L:D ratio</u>: Bao et al. [83] reported a decrease in D_{CO_2} at 30 °C and 0% RH when L-lactide increases from 50 to 80%, and an increase in D_{CO_2} at the same test conditions when L-lactide increases from 80 to 98%. Sawada et al. [143] and Komatsuka et al. [205] reported D_{CO_2} at 35 °C, 0% RH and the data show an increasing trend from 0% to 20% X_c and a decreasing trend from 20% to 40% X_c . Explanation of this behavior is later provided in the oxygen section (Section 2.6).

2.5.3 Solubility

Figure 2-15 shows an Arrhenius plot of *S* (based on Eq. 25) for O₂, CO₂, N₂, and CH₄ in PLA films at dry conditions. Overall, *S* of these gases is lower than 4.9×10^{-4} kg.m⁻³.Pa⁻¹ below T_g . To date, there are no reports of *S* of these gases above T_g . A large dispersion of the data may be due to different methods of testing and film processing as well as film defects.

Sawada et al. [143] reported that *S* follows the decreasing trend of $CO_2 > CH_4 > O_2 > N_2$, in line with the gas critical temperature (*T_c*). Our data show different trends in Figure 2-16. However, as discussed in the permeability section, once the unit of *S* is expressed in mass (kg.m⁻³.Pa⁻¹) instead of volume (cm³(STP). cm⁻³.cmHg⁻¹), the trends become similar. *S* values of ClO₂ (*S_{ClO2}*) was reported as 1.90±0.15×10⁻³

kg.m⁻³.Pa⁻¹ at 23 °C and 50% RH [146], which is higher than the reported S of other gases.



Figure 2-15 Arrhenius plot of solubility coefficients (*S*) for O₂, CO₂, N₂, and CH₄. Data references: O₂ \triangleleft [193], \checkmark [133], * [83,143,148,166,168,176,205]. CO₂ \circ [193], \Box [230], \diamond [228], \triangle [83,143,176,205]. N₂ \bullet [193], \diamond [83,143,205,231]. CH₄ + [143]. Each dashed line represents a least squares linear regression of each gas from the reported experimental data.



Figure 2-16 Plot of average solubility coefficient (*S*) values, with standard error bars, as a function of critical temperature (T_c) of different gases for neat PLA at 20–35 °C and 0% RH [83,133,143,166,168,176,193,205,228,230,231], except for S_{ClO_2} which was measured at 50% RH [146]. The dashed line is a linear trend line for ln(*S*) versus T_c . The coefficient of determination (r^2) is 0.8236.

Effect of temperature: As reported in Table 2-4, at 0% RH ΔH_S of CO₂ estimated from sorption data from Oliveira et al. [193] was -21.88 kJ.mol⁻¹ for PLA 80% L with 0% X_c at 20–40 °C. Similarly, using sorption data from Oliveira et al. [228], ΔH_S of CO₂ for PLA 98% L and 20% X_c was estimated as -23.14 kJ.mol⁻¹ at 10–40 °C. Moreover, other experimental data from the same group of authors [229,230] at 30–50 °C, 0% RH were used to estimate ΔH_S of CO₂ for PLA 98% L, 20% X_c and PLA 80% L, 0% X_c , which yielded ΔH_S values of -21.58 kJ mol⁻¹ and -22.22 kJ mol⁻¹, respectively. Bao et al. [83]

reported ΔH_S of CO₂ for PLA films with different L-lactide contents at 23–45 °C and 0% RH. They reported ΔH_S values for PLA with 50, 80, and 98.7% L as -25.4, -13.9, and -18.4 kJ.mol⁻¹, respectively. To date, the only available ΔH_S data for PLA are for CO₂ below T_g and the values reported are between -25 and -14 kJ.mol⁻¹. Data on the effect of temperature on *S* for other gases below T_g , as well as for all gases above T_g are still lacking.

<u>Effect of relative humidity</u>: No reports of experiments on the effect of RH on S were found. At high RH, water vapor from the environment could fill the FV in PLA and thus reduce the available space for gases to solubilize. Therefore, additional research is needed to further address the effect of RH.

<u>Effect of crystallinity and L:D ratio</u>: Data from selected authors [83,193,229,230] suggest that *S* increases as % L-lactide increases and decreases as crystallinity increases. While the result is contradictory since generally crystallinity increases as L-lactide increases, this can be attributed to different processing techniques and the presence of RAF as will be discussed in Section 2.6.

2.5.4 Effect of modification

Figures 2-17a), b), and c) show the effects of PLA film modifications for P_{CO_2} [173,186], P_{N_2} [156,167,179,216,232], and P_{He} [163,165,168,191], respectively. The negative % change values indicate increased barrier compared to the original unmodified PLA. PLA with nanocomposites and blends showed a decrease in *P* values while PLA with

additives showed varying results depending on the type and the concentration of the additives. Ortenzi et al. [186] studied the effects of nanoparticle shape and surface modification on crystallinity, and gas and vapor barrier properties. They used two types of nanoparticles: nanosilica (NS) and organically-modified montmorillonite (OMMT), with amino silane (3-aminopropyltriethoxysilane) or epoxy silane (3-

glycidoxypropyltrimethoxysilane) added to improve polymer-nanoparticle compatibility. They found that the presence of nanoparticles, especially when modified with silanes, greatly enhanced barrier properties to CO_2 where P_{CO_2} was reduced up to 50%. For NS, the authors reported an improvement in gas barrier properties with the addition of silane, especially for epoxy silane. They attributed this result to an enhanced crystallization process with the presence of silane. However, in the case of OMMT, the addition of silane did not improve gas barrier properties. Siracusa et al. [173] studied barrier properties of PLA with various surface treatments (silicon oxide (SiOx) coated, anti-UV coated, and varnished) and found that PLA with surface treatments showed much better barrier properties to O_2 and CO_2 than unmodified PLA. Several authors studied PLA modifications with nanoclays [156], NS [167], graphene oxide and graphene nanoplatelets [179] and reported improvement in barrier to N_2 . When using additives such as poly(ethylene glycol) (PEG) [163] or acetyl tributyl citrate (ATBC) [163,168], the results varied depending on the amount of additives added. Blending PLA with poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) resulted in a better barrier to He, as compared with neat PLA [191]. Besides the data shown in Figure 2-17, Samuel et al. [216] reported enhanced barrier to N_2 for PLA blended with petro-based poly(methyl methacrylate) (PMMA) and Picard et al. [165], studying the effect of OMMT

on PLA crystallization and gas barrier properties, reported an improvement of barrier to He with the presence of OMMT. It is apparent that the barrier properties of PLA can be improved or tailored as needed, with some limitations. This opens an opportunity to use PLA in wider applications where barrier properties are crucial.



Figure 2-17 Effects of PLA film modifications on a) P_{CO_2} , b) P_{N2} , and c) P_{He} . References: ^a [186], ^b [173], ^c [156], ^d [167], ^e [179], ^f [191], ^g [163], ^h [168]. The numbers on top and bottom of the bars are $P(10^{-18} \text{ kg.m.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1})$ of neat PLA used in the corresponding experiments. (+) change means increasing P (worse barrier) and (-) change means reduction of P (better barrier). Abbreviations: NS = nanosilica, a-Si = amino silane, e-Si = epoxy silane, OMMT = organically-modified montmorillonite, C = Cloisite[®], GO = graphene oxide, GNP = graphene nanoplatelets, PMMA = poly(methyl methacrylate), PHBV = poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate), PEG = poly(ethylene glycol), ATBC = acetyl tributyl citrate.

2.5.5 Data gaps and recommendations

Extensive research has been conducted regarding the *P* of O₂, CO₂, N₂, and H₂ below and above T_g . However, He and CH₄ have only been investigated below T_g . There is no clear correlation between *P* and M_W , *D* and V_c , or *S* and T_c , but the assumption that M_W and V_c affect *D* and *S*, which results in the change in *P*, should be investigated. *E_P* values have been reported for O₂, N₂, CO₂, and H₂ below and above T_g , but *E_P* values for CH₄ and ClO₂ have only been reported below T_g . *E_P* average values were estimated for H₂, CO₂, and N₂ below and above T_g at 0% RH, and for He below T_g at 0% RH. No average value has been reported for CH₄. The effect of RH on *P* of the gases has not yet been fully investigated. The effect of crystallinity on *P* of most gases is not clear, mostly due to lack of consideration of the three-phase morphology (i.e., CF, MAF, and RAF) as later explained for O₂.

For PLA, a linear relationship between *D* and *V_c* could be tentatively established for gases. However, trends for the relationship between *S* and *T_c* could not be established. Different scaling laws between *D* and molecular sizes of gases [17], as well as between *S*, *T_c*, and gas condensability [231,233–236], in other polymers have been discussed in the literature. Additional work under controlled experimental conditions is needed to fully understand these relationships in PLA. Furthermore, the effect of PLA modifications on *P*, *D*, and *S* of gases is not yet totally understood. In the case of nanoparticles, most researchers attributed the improvement of *P* to the reduction of *D* caused by increased tortuosity. However, experimental data showed large variability. Therefore, a unified theory about the effect of particle and nanoparticle size, shape and chemistry is still out of reach.

2.6 Mass transfer of oxygen

Oxygen barrier properties through PLA films have been extensively studied [58,59,63,83,133,143–145,147–188,192–224]. O₂ is often used as a probe for understanding the impact of modifications on barrier properties. In the following section, we provide a detailed discussion of *P*, *D*, and *S* for O₂. Interestingly, some studies of O₂ barrier helped to elucidate the crystalline structure of PLA [132,133,168,232]. Several additional studies have reported the O₂ barrier properties of PLA [145,211,216,237], but their units or information were incomplete or insufficient for comparison with other reported measurements in this review.

2.6.1 Permeability

 P_{O_2} values in PLA films [58,59,83,133,143,144,147–167,169–188,195,198,200– 202,206,207,209,210,213,214,217,218,221–223,238] are summarized in Figure 2-18. Most of the values between 5 and 58 °C are aggregated around $0.5\pm0.7\times10^{-17}$ kg.m.m⁻².s⁻¹.Pa⁻¹. Values from Lehermeier et al. [145] are excluded in this discussion as previously explained. In general, there is considerable variability in the measured P_{O_2} values. All the *P* values were reported to follow Fick's laws of diffusion. As expected, an increase rate in P_{O_2} is observed above T_g implying a discontinuity in the Arrhenius relationship across glass-rubber transition as discussed in Section 2.4.4.



Figure 2-18 Oxygen permeability coefficients (P_{O_2}) of PLA between 5 and 90 °C and 0 and 100% RH. Data references: 0% RH ∘ [133], □ [147], △ [144], ◊ [58,59,83,143,148– 167,169–188]. 1–49% RH * [148], ▽ [175,202,210]. 50–79% RH • [63], ■ [222], ▲ [148], • [158,175,188,198,200,201,213,214,217,218,221]. 80–100% RH ▷ [148], + [153,166,195,206,207,209,223,238]. The vertical dashed line is an arbitrary T_g of 58 °C.

<u>Effect of temperature</u>: An increase in P_{O_2} with temperature is observed for all the values, following the Arrhenius equation (Eq. 23). Most values were reported at 0% RH. Auras et al. [63,148] studied the effect of temperature for PLA 94% L and 98% L. They reported activation energies of permeation of O_2 (E_{P,O_2}) at 70% RH and 25–45 °C for PLA 98% L-lactide and PLA 94% L-lactide as 41.4±3.5 kJ.mol⁻¹ and 28.4±2.9 kJ.mol⁻¹, respectively [63]. In a later work, the same group of authors [148] estimated E_P , E_D and ΔH_S of O₂ at 5–40 °C and 0–90% RH for the same PLA polymers and reported the average E_{P,O_2} across all the RH conditions (0, 30, 60, and 90% RH) for PLA 98% L of

23.39±1.11 kJ.mol⁻¹, and for PLA 94% L of 20.46±1.57 kJ.mol⁻¹. Flodberg et al. [222] measured oxygen barrier properties of PLA at 50% RH and 23, 28, 33, and 38 °C, and reported E_{P,O_2} of 45.1 kJ.mol⁻¹. Komatsuka and Nagai [144] studied the effect of temperature above T_g between 45 and 85 °C in PLA with different amounts of L and D content, and reported E_{P,O_2} crossing T_g of 47.9 kJ.mol⁻¹. They reported a linear trend of P across T_g for two types of PLA: 96% L PLA homopolymer and blends of 96% L and 88% L at 8:2 ratio. However, as observed in Figure 2-18, a change in the slope of ln(P) versus the reciprocal of temperature is observed at T_g for the overall experimental determinations. Table 2-6 shows the E_P , E_D , and ΔH_S of O₂ in PLA below and above T_g at different RH for the aggregated values presented in Figure 2-18, as well as from individual values reported in the literature.

Temperature	RH, %	PLA	E _{P,}	E _{D,}	$\Delta H_{S,}$	Ref.
range, °C			kJ.mol ^{−1}	kJ.mol⁻¹	kJ.mol ^{−1}	
25–45	70	98% L	41.4±3.5	n/a	n/a	[63]
25–45	70	94% L	28.4±2.9	n/a	n/a	[63]
5–40	0–90	98% L	23.39±1.11	0.96–4.97	16.94–22.65	[148]
5–40	0–90	94% L	20.46±1.57	5.05–28.04	n/a	[148]
23–38	50	n/a	45.1	45.2	-0.074	[222]
23–30	0	98.7% L	24.0	42.7	-19.2	[83]
23–30	0	80% L	24.9	40.8	-15.9	[83]
23–30	0	50% L	26.6	68.8	-42.0	[83]
45–85	0	96% L	47.9	n/a	n/a	[144]
45–85	0	96%:88% L blends	41.4	n/a	n/a	[144]
5–58	0	(various)	21.8±6.0	28.2±21.2	26.7±16.3	This
5–58	1–49	(various)	19.6±9.0	7.8±16.3	12.4±20.4	This
5–58	50–79	(various)	18.9±8.6	58.0±35.6	-40.3±40.8	This
5–58	80–100	(various)	18.8±4.8	14.8±31.9	-4.9±39.9	This review
59–90	0	(various)	44.5±13.7	n/a	n/a	This review

Table 2-6 Average values of E_P , E_D , and ΔH_S of O₂ in PLA below and above T_g estimated from literature data [58,59,63,83,143–145,147–188,192–224] as presented in this review, as well as values reported in the literature.

n/a: not available

Effect of relative humidity: Although PLA is susceptible to hydrolysis when exposed to moisture for a long period of time, overall P_{O_2} values (Figure 2-18) do not show any correlations with RH, implying that short-term exposure to humidity does not affect P_{0_2} of PLA. However, this may be due to the variability of the reported P_{O_2} . Auras et al. [148] studied biaxially oriented PLA 94% L and 98% L films at 5, 23, and 40°C at 0, 30, 60, and 90% RH. The authors did not find any effects of RH below room temperature (23 °C). However, they reported a decrease in P_{O_2} as RH increased for both films at 40°C. Cho et al. [158] measured P_{O_2} of PLA 94% L at 23 °C and did not report any changes of Po2 when RH increased from 0 to 50% RH. Fukuzumi et al. [175] also studied oxygen barrier properties of PLA films at 23 °C and 0, 35, 50, and 75% RH, and did not find any significant differences in Po2 with RH. Yang et al. [188] studied PLA with 96% \perp (PLA 5200D, 2% X_c) at 23°C and also did not find any significant differences in Po2 between 0 and 50% RH. Therefore, as long as PLA specimens are not being hydrolyzed, RH seems not to influence P_{O_2} of PLA at low temperature. However, one paper reported a decrease in Po2 as RH increased at temperatures higher than 40°C [148]. As a result, further studies on the effects of both temperature and RH are recommended for better understanding of PLA barrier properties.

<u>Effect of crystallinity and L:D ratio</u>: PLA with L-lactide higher than 92% is a semicrystalline polymer, the crystallinity of which depends on the processing technique. Researchers used different processing methods such as solvent casting, extrusion, quenching, annealing, blowing, and orientation to produce PLA films of different

crystallinity. Although crystalline regions are generally impermeable to gases, Guinault et al. [161] could not determine whether the recrystallization process of PLA with 99% L and PLA with 98% L had any effect on barrier properties. However, they showed that P_{O_2} decreased when X_c increased more than 40% for PLA with 99% L and monotonically decreased for PLA with 98% L. Byun et al. [215] also produced PLA films with different X_c (14, 24 and 46%), and found that films greater than 30% X_c showed lower P_{O_2} . On the other hand, other authors [148,205] reported that PLA with high X_c (~40%) showed higher P_{O_2} than PLA with lower X_c . Komatsuka et al. [205] attributed this behavior to the size and distribution of FV in crystalline PLA membrane. The inconsistent trends reported in the literature imply that the relationship of P_{O_2} and X_c of PLA cannot be explained simply based on crystalline domains (Eq. 20). Bao et al. [83] found differences in P_{O_2} for different percentages of L-lactide; the higher the L-lactide content, the higher the *P* value. However, this observation is also inconsistent with the fact that PLA with higher L-lactide tends to have higher X_c .

Courgneau et al. [168] showed that P_{O_2} increased slightly with X_c . The authors also did not find a change of the *D* values of $O_2 (D_{O_2})$ with X_c , and they attributed this unusual behavior to the presence of three phases (i.e., CF, RAF, and MAF) in PLA. The reason could be the de-densification of the amorphous phase or the formation of the RAF created by PLA crystallization. In another study, the same authors [133] reported that D_{O_2} increased until 40% X_c and then decreased (Figure 2-19b). Although there is a monotonic reduction of the *S* values of $O_2 (S_{O_2})$ with an increase of crystallinity, a reduction of P_{O_2} is not observed due to the compensating effect of increasing D_{O_2} (Figures 2-19a and d). Similar trends are observed in Figures 2-19d, e, and f which

show the average P_{O_2} , D_{O_2} , and S_{O_2} at 20–30 °C, 0% RH from this review.

Sato et al. [232] recently quantified the RAF and the crystallinity in PLA samples annealed at different temperatures, and confirmed that the gas diffusivity and permeability in PLA films depended on both the amount of RAF and *X_c*. The density of the RAF is close to that of lamellar crystals, so the high density and low mobility of the RAF might have restricted the gas diffusion and permeation in the PLA films. However, results from these authors showed that RAF had a higher density than MAF, which contradicted recent findings from other studies [128,132–134]. Therefore, interpretation of results should proceed with caution. A recent study [132] demonstrated that the formation of RAF in the amorphous phase hindered the relaxation of the polymer chains and therefore increased the FV, thereby providing an accelerated pathway for diffusion. Hence, when studying the mass transfer in semicrystalline PLA, the three-phase model must be considered.



Figure 2-19 a–c) *P*, *D*, and *S* values of O₂ measured at 23 °C and 0%RH adapted from Guinault et al. [133] with symbols indicating time/temperature conditions of the crystallization treatment for PLA: \diamond extruded sample, \bullet 85 °C, \blacksquare 90 °C, \blacktriangle 120 °C, \times 140 °C. d–f) *P*, *D*, and *S* values of O₂ (shown with \diamond symbol) at 20–35°C and 0% RH reported in this review.

To improve the barrier properties of PLA using a unique approach, Bai et al. [239] induced parallel-aligned shish-kebab-like crystals with well-interlocked boundaries in PLA with 98% \perp by using a highly active nucleating agent. They found that instead of an increase in X_c , the type of crystal structure formed, in this case densely packed nanobrick wall structures, was responsible for a reduction of P_{O_2} from 7.4×10⁻¹⁸ kg.m.m⁻².s⁻¹.Pa⁻¹ for PLA with 50% X_c to 2.7×10⁻²⁰ kg.m.m⁻².s⁻¹.Pa⁻¹ for PLA with 0.5 wt% of N,N',N"-tricyclohexyl-1,3,5-benzene-tricarboxylamide (TMC-238) which had 48% X_c . Auras et al. [149] studied how the introduction of recycled PLA affected P_{O_2} and found oriented PLA (OPLA) with 40% regrind had P_{O_2} twice as high as P_{O_2} of virgin OPLA. While the results from these studies show that recycled PLA may not be a good choice for applications that require high barrier properties, there are possibilities to enhance barrier of PLA using various viable methods.

2.6.2 Diffusion

Consolidated D_{O2} data from the literature for PLA films

[83,143,148,163,165,166,168,176,180,200,203,205,222,223] are summarized in Figure 2-20. The plot shows that D_{O_2} values below T_g range from 1.8×10^{-14} to 841×10^{-14} m².s⁻¹, indicating a high variation which could be attributed to different measurement and processing methods used between studies, as well as different crystalline and amorphous domains produced in the test specimens that affect the tortuous paths for O_2 molecules to diffuse through the film. Different film processing methods can create PLA films with different amounts of the RAF. An increase in the number of voids with smaller FV in the RAF through annealing can lead to higher diffusion of O_2 molecules. If the solubility remains unchanged, the higher diffusion will result in higher permeation. However, with the observed high variations in the reported D_{O2} values, further studies with better-controlled experimental conditions are required.



Figure 2-20 Oxygen diffusion coefficients (D_{O2}) of PLA between 5 and 40 °C and 0 and 100% RH. Data references: 0% RH \circ [148], \Box [133], Δ [83,143,163,165,166,168,169,176,180,205]. 1–49% RH * [148]. 50–79% RH \triangleleft [148], ∇ [222], \Diamond [200]. 80–100% RH \triangleright [148], + [166,223,238].

Effect of temperature: Several authors [83,148,222] show that plots of $\ln(D_{O_2})$ versus the reciprocal of temperature follow the Arrhenius equation (Eq. 24). However, the values are greatly different between studies. Auras et al. [148] reported activation energy of diffusion of O₂ (E_{D,O_2}) of 1.0 to 5.0 kJ.mol⁻¹ for PLA 98% L (4031D) and 5.0 to 28.0 kJ.mol⁻¹ for PLA 94% L between 5 and 40°C and 0 to 90% RH. Flodberg et al. [222] reported E_{D,O_2} of 45.2 kJ.mol⁻¹ from the range of 23–38 at 50% RH. Bao et al. [83] reported D_{O_2} at 23 and 30 °C for dry conditions and annealed films at which E_{D,O_2} was estimated as 42.7 kJ.mol⁻¹ for PLA 98.7% L, 40.8 kJ.mol⁻¹ for PLA 80% L, and 68.8 kJ.mol⁻¹ for PLA 50% L. Table 2-6 shows the reported E_{D,O_2} values from the literature, as well as the average E_{D,O_2} values estimated from this review. At 0% RH, the average E_{D,O_2} below T_g from this review is 28.2±21.2 kJ.mol⁻¹. Compared to the reported values, the estimated E_{D,O_2} from this review is fairly low, but it could be a result of high variability of D_{O_2} , especially at room temperature (23 °C) where the majority of data on D_{O_2} were reported.

<u>Effect of relative humidity</u>: Auras et al. [148] reported an increase in E_{D,O_2} as RH increased, indicating that temperature had stronger effect on D_{O_2} at higher RH. However, this was not reflected in the *P* values due to a relative compensation between *D* and *S*. At 24 °C, Sanchez-Garcia et al. [166] reported slightly higher D_{O_2} at 80% RH than at 0% RH.

<u>Effect of crystallinity and L:D ratio</u>: Auras et al. [148] reported D_{O_2} values for PLA films with 98% L and 94% L. The results showed that at dry conditions, PLA with 98% L (25% X_c) had lower D_{O_2} than PLA with 94% L (40% X_c) at 5 °C. However, as the temperature increased to 40 °C, D_{O_2} values for both PLA films were not much different, with PLA 98% L showing slightly higher D_{O_2} than that of PLA 94% L. Sawada et al. [143] reported an increase in D_{O_2} when X_c increased from 0% to 20% and a decrease in D_{O_2} when X_c increased from 20% to 40%. Picard et al. [165] reported a decrease of D_{O_2} from 14.2×10⁻¹³ to 7.96×10⁻¹³ m².s⁻¹ at 20 °C and 0% RH when PLA film was annealed, which resulted in an increase in X_c from 0 to 46%. Courgneau et al. [168] reported D_{O_2} for non-annealed 92% L PLA films (3% X_c) and 92% L PLA films (36–43% X_c) recrystallized at different temperatures and found no difference in D_{O_2} values for these films. Bao et al. [83] reported that at dry conditions, PLA with 98% L (~40% X_c) and PLA 80% L (0% X_c) had very similar D_{O_2} values, while PLA with 50% L (0% X_c) had higher D_{O_2} . Guinault et al. [133] reported an increase in D_{O_2} for PLA with 96% and 99% L when X_c increased from 2% up to 40% and a decrease in D_{O_2} at higher X_c , showing the same behavior as their reported P_{O_2} . Komatsuka and Nagai [144] reported D_{O_2} at dry conditions for homopolymer PLA 98% L as higher than D_{O_2} for blends of 96% L and 88% L at 8:2 ratio.

Del Río et al. [134] studied the evolution of FV in crystallized PLA with 98% L and postulated that upon annealing the PLA, there was an increase of FV located inside the RAF. Annealing led to a decrease in the FV void sizes while the quantity of the voids increased. The increase in the number of small voids can lead to higher diffusion of O₂ molecules, which results in high permeation. Fernandes Nassar et al. [132] also found an accelerated pathway for diffusion of small molecules such as O₂ due to the occurrence of RAF and thereby the increase of FV.

2.6.3 Solubility

Values of S_{O_2} in PLA films have been reported [83,143,148,166,168,176,193,200,203,205,222,223] and are shown in Figure 2-21. S_{O_2} values measured or estimated between 5 and 40 °C have been reported with an

average of $4.23\pm8.04\times10^{-5}$ kg.m⁻³.Pa⁻¹. Values of S_{O_2} reported in the literature differ by many orders of magnitude, ranging between 2.36×10^{-7} and 4.88×10^{-4} kg.m⁻³.Pa⁻¹ at 5 to 40 °C and 0 to 90% RH. These variations could be attributed to differences in PLA sources, processing, measuring methods, and different amounts of induced RAF. Some authors [143,148,166,168,176,205] estimated *S* from Eq. 7, while some authors [222] used Eq. 8, and others [193] measured *S* directly using QCM. Therefore, dependable S_{O_2} values with respect to temperature, RH, and X_c for PLA are still lacking.



Figure 2-21 Oxygen solubility coefficients (S_{O_2}) of PLA between 5 and 40 °C and 0 to 90% RH. Data references: 0% RH \circ [148], \Box [133], Δ [83,143,166,168,176,193,205]. 1–49% RH * [148]. 50–79% RH \triangleleft [148], ∇ [222], \diamond [200]. 80–100% RH \triangleright [148], + [166,223,238].

Effect of temperature: Auras et al. [148] reported S_{O_2} between 5 and 40 °C and 0 to 90% RH. They reported ΔH_S between 16.9 and 22.6 kJ.mol⁻¹. Oliveira et al. [193] reported S_{O_2} between 20 and 40 °C and pressure 0.11 to 0.995 bar and fit the experimental values to the Flory-Huggins model, Eq. 9. Bao et al. [83] reported ΔH_S between -15.9 to -42.0 kJ.mol⁻¹ for PLA with 50–98.7% L. On the other hand, Flodberg et al. [222] estimated a ΔH_S value of -0.1 kJ.mol⁻¹. Furthermore, using Eq. 8, they decoupled the contribution of ΔH_S and indicated that the contribution of ΔH_C is negligible for O₂ mass transfer. So, the main contributor is ΔH_m , which is always negative for condensable gases. The linear regression lines of the overall S_{O_2} data (Figure 2-21) did not yield reliable values of ΔH_S values from literature also show high variability, which could be due to differences in PLA sources and processing conditions, as well as differences in measurement methods.

<u>Effect of relative humidity</u>: A linear decrease in S_{O_2} as RH increased to 90% for PLA with 98% L was reported by Auras et al. [148]. They also reported a decrease in ΔH_S as RH increased from 0 to 90%. Sanchez-Garcia et al. [166] reported slightly lower S at 80% RH than at 0% RH. However, no extensive research has been conducted on the effect of RH on S_{O_2} .

<u>Effect of crystallinity and L:D ratio</u>: Auras et al. [148] studied S_{O_2} in PLA with 98% L (40% X_c) and PLA with 94% L (25% X_c) and reported a decrease in S_{O_2} as X_c increased.

Sawada et al. [143] reported a slight reduction of S_{O_2} as X_c increased from 0 to 40%. Komatsuka et al. [205] also observed a decrease in S_{O_2} from 1.53×10^{-6} to 8.5×10^{-7} kg.m⁻³.Pa⁻¹ when X_c was changed from 7.4 to 24.8%. Courgneau et al. [168] also found a decrease in S_{O_2} from 2.43×10^{-6} to 1.00×10^{-6} kg.m⁻³.Pa⁻¹ when X_c increased from 3 to 43%. So, these few reports seem to indicate that S_{O_2} should decrease when X_c increases, which is expected for most polymers.

2.6.4 Effect of modification

To overcome PLA's poor or medium barrier to O_2 , many researchers have modified PLA by using a number of additives [162,163,168,169,171,176,194,199,221,240], blending with a number of bio-based and fossil-based polymers [149,151,157,166,182,188,203,212,216,223], or compounding with fibers, micro- and nanoparticles [58,59,150,156,165,170,174,175,177–180,183–186,198,200–203,206, 207,209,210,212,213,217–219,223]. Figure 2-22 shows percentage changes of P_{O_2} due to such modifications. It is clear that not every modification improves PLA's barrier properties.

The incorporation of additives such as ATBC [168] into PLA did not improve PLA O_2 barrier. The addition of 2 wt% talc to PLA slightly improved O_2 barrier; however, formulated PLA with 1 wt% talc and 17 wt% ATBC did not improve O_2 barrier and showed 95% increase in P_{O_2} [168]. Plasticization effects of carboxyl and hydroxyl PLA monomers [182] resulted in higher P_{O_2} of the blends of PLA and the monomers. However, physical aging of neat PLA as well as the blends (data not shown) was reported to improve PLA barrier to O_2 [182]. Blending PLA with poly(butylene succinate-

co-adipate) (PBSA) increased Po2, but coupling PBSA to crotonic acid functionalized PLA resulted in branched plasticized PLA which significantly reduced Po2 [188]. Sanchez-Garcia et al [166] reported a reduction in Po2 at 24 °C and 0% RH in PLA/ethylene vinyl alcohol (EVOH) blends. Since gas permeability for the blend films is determined by the volume fractions of the polymer components, and since EVOH is hydrophilic, P_{02} will be higher in the blends due to swelling of EVOH when exposed to water. However, at 24 °C and 80% RH (data not shown), the authors reported that blending EVOH with PLA did not reduce P_{0_2} and the reason for no O_2 barrier improvement was due to the interaction of the blends with water. The same researchers also found the addition of amylopectin (AP) to PLA/EVOH blends slightly decreased Po2 at 0% RH, but increased P_{O_2} at 80% RH. The addition of nanoparticles such as montmorillonite (MMT) [186], modified MMT [153], OMMT [165], TiO₂ [213], NS [186], NS and silanes [186] reduces P_{O_2} between 15 to 100%. However, the addition of laurate-intercalated Mg-Al layered double hydroxide (LDH-C₁₂) as a nanofiller increases P_{O_2} , which could be due to PLA degradation as will be discussed in Section 2.7.4. Regarding nanoparticles, many authors claimed to obtain an intercalated or exfoliated structure of the layered silicates; however, most of the structures were predominantly intercalated [151,154,208,214,241,242].



Figure 2-22 Change of PLA P_{O_2} due to the introduction of additives, blending or compounding with micro- and nanoparticles. The numbers on top and bottom of the bars are P_{O_2} (10⁻¹⁸ kg.m.m⁻².s⁻¹.Pa⁻¹) of neat PLA used in the corresponding experiments. (+) change means increasing *P* (worse barrier) and (-) change means reduction of *P* (better barrier). References: a [153], b [213], c [214], d [186], e [165], f (annealed PLA) [165], g [182], h [188], i [166], i [168]. Abbreviations: modified MMT = modified montmorillonite, LDH = layered double hydroxide, NS = nanosilica, NS/aminoSi = nanosilica/amino silane, NS/epoxySi = nanosilica/epoxy silane, MMT = montmorillonite, MMT/aminoSi = montmorillonite/amino silane, MMT/epoxySi = montmorillonite/epoxy silane, OMMT = organically-modified montmorillonite, hydroxyl o-LA = hydroxyl lactic acid oligomer, carboxyl o-LA = carboxyl lactic acid oligomer, PBSA = poly(butylene succinate-co-adipate), CA-PBSA = crotonic acid functionalized poly(lactic acid) coupling poly(butylene succinate-co-adipate), EVOH = ethylene vinyl alcohol, E29+50%AP = blends of EVOH 29% and AP (amylopectin) 50%, ATBC = acetyl tributyl citrate.

2.6.5 Data gaps and recommendations

Robust data to elucidate the effects of RH on PLA film O2 barrier properties at different

temperatures are lacking. A thorough understanding of the simultaneous mass transfer

mechanisms of O₂ and H₂O in PLA films is needed. Further studies are recommended

for O₂ barrier properties of PLA from 0–100% RH and 5–50 °C. There are some studies

looking at the effects of crystallinity on O₂ barrier properties and reporting that as Llactide content increases so does the crystallinity, but the O_2 barrier properties are weakened. This trend is unexpected since crystalline regions are not permeable to permeant molecules. An initial explanation of this phenomenon was given based on the formation of a three-phase structure (CF, MAF and RAF) and de-densification of the amorphous phase. By controlling morphology and size of spherulites, Fernandes Nassar et al. [132] established that the RAF is a major factor affecting PLA's barrier properties. Similarly, Bai et al. [239] demonstrated how specific crystalline architectures could affect PLA barrier properties. However, the effect of the amorphous phase remains elusive; further studies on the amorphous phase structures of PLA are needed. It seems that although researchers can control the amount of crystallinity in PLA, they cannot fully control the type of crystal regions formed, which seem to have a substantial effect on PLA O₂ barrier properties. So, special attention should be given to fully characterize the PLA structure to be able to extrapolate the reported results to other conditions. It is unclear what are the main effects of crystallinity on P_{0_2} of PLA. It seems that crystallinity level is not the only factor in controlling P_{O_2} . Further studies should be conducted to understand whether the type of crystals and the amount of MAF and RAF play a significant role.

Few D_{O_2} values in PLA have been reported. Additional work is needed to further understand the diffusion behavior. The effects of the following factors still need to be elucidated: a) L and D-LA content ratio; b) crystallinity; c) temperature; d) orientation. Additional study of S_{O_2} should be carried out to fully understand the amount of oxygen dissolved in PLA under different environmental conditions. This information is critical for

understanding PLA oxidation at high temperature. Most researchers have modeled solubility of O₂ in PLA following Henry's law (Eq. 7). Only one study [222] used the Henry-Langmuir sorption approach (Eq. 8). Further studies should be conducted to fully understand which model better describes the sorption of O₂ in PLA. The simultaneous solubility of O₂ with different gases should be assessed to elucidate their synergistic or antagonistic effects on the barrier properties of PLA.

2.7 Mass transfer of water vapor

Several researchers have studied P, D, and S of water vapor. In general, P and D increase when temperature increases with some exceptions [63], while S always decreases with increasing temperature. Due to the antagonistic effect of D and S (i.e., increase in D and decrease in S as temperature increases), P is not affected much by temperature. Overall values of P, D and S do not exhibit increasing or decreasing trend when RH increases. However, water vapor diffusion in PLA and its nanocomposites is reported to follow non-Fickian behavior [21,73]. Regarding how crystallinity affects P, D and S values, experimental results from different authors appear to be contradictory, attributable to the two different amorphous regions in PLA, i.e., MAF and RAF. However, at the time of the studies, most researchers did not characterize the CF, MAF and RAF of their PLA specimens. There is also a report [243] that in biaxially drawn PLA films, crystallinity degree was not the main factor affecting barrier property to water vapor, but the increase in the tortuous path from the drawing process reduced water diffusivity and thus improved water vapor barrier. Furthermore, water cluster formation, which is another phenomenon that can further affect the water transport process, has

been reported by researchers who investigated *S* of water in PLA [244–246]. Specific details of the studies and findings for each parameter are discussed below.

2.7.1 Permeability

Figure 2-23 shows Arrhenius plots of *P* values for H₂O (P_{H_2O}) [56,58,62,63,65,147, 149,158,163,171,172,174,176,181,184,192,195–197,247–260] in a range from 1.1×10⁻¹⁹ to 1.2×10⁻¹³ kg.m.m⁻².s⁻¹.Pa⁻¹. The majority of the values fall between 10⁻¹⁶ and 10⁻¹³ kg.m.m⁻².s⁻¹.Pa⁻¹. The large dispersion of the data may be due to different film processing and measurement methods. Moreover, some values of P_{H_2O} were estimated from the relationship P = DS where D and S were measured separately. The low P_{H_2O} values in the range of 10⁻¹⁸ to 10⁻¹⁶ kg.m.m⁻².s⁻¹.Pa⁻¹ reported by Gulati [89] are a result of very low D values, which will be discussed later in Section 2.7.2.



Figure 2-23 Arrhenius plot of water vapor permeability coefficients (P_{H_2O}) of PLA between 6 and 50 °C grouped by different relative humidity (RH) ranges. Each dashed line is from linear regression of the data in each RH range group. References: 1–49% RH ■ [172], ▼ [89], × [153,166,175,176,261–263]. 50–79% RH \circ [56], * [63], △ [42,62,65,89,162,163,172,174,178,182,183,185,197,202,213,252,255,256,258,264– 268]. 80–100% RH \diamond [56], ▷ [147], □ [254], <] [269], + [58,89,149,150,152,158,163,171,172,175,184,186,195,214,222,223,247– 251,253,257,259,270–276].

<u>Effect of temperature</u>: Auras et al. [63] found that P_{H_2O} decreased as temperatures increased from 10 to 38 °C, which is counterintuitive. However, this observation is in accordance with the three-phase model, wherein the de-densification of the RAF domain in PLA tends to decrease as temperature increases. This observation implies that the FV does not increase to the same extent as the increase in mobility of the

chains with increasing temperature. The decrease in diffusion can result in a reduction in P_{H_20} within this narrow temperature range. The activation energy of permeation of H₂O (E_{P,H_20}) was studied for two PLA films with different X_c at temperatures between 10 and 38 °C and the reported E_{P,H_20} values for PLA film with 40 and 25% X_c were -9.8 and -10.1 kJ.mol⁻¹, respectively [63]. Furthermore, Siparsky et al. [56] and Shogren et al. [247] reported E_{P,H_20} values of amorphous and semicrystalline PLA of 5 and -0.1 kJ.mol⁻¹, respectively. Since condensation is an exothermic process, the value of ΔH_c is always negative. For E_P to be negative ΔH_M must be lower in absolute value than ΔH_{C_r} and E_D must be smaller than the absolute value of the sum of ΔH_M and ΔH_C , according to Eqs. 26 and 27. Table 2-7 shows E_P , E_D , ΔH_S , ΔH_C , and ΔH_M for different PLAs. The averages are plotted at different humidity values in Figure 2-23. Low ΔH_M for groups of data with different RH values may be attributed to variation in materials and measurements.

PLA sample	<i>E</i> _P , kJ.mol ^{−1}	<i>E</i> _D , kJ.mol ^{−1}	∆H _S , kJ.mol ⁻¹	ΔH_{C} , kJ.mol ^{-1,a}	ΔH_M , kJ.mol ^{-1,b}	Ref.
50% ∟-lactide	30	62	-32	-42	10	[56]
70% ∟-lactide	5	24	-19	-42	23	[56]
90% ∟-lactide	7	26	-19	-42	23	[56]
95% ∟-lactide, <i>M</i> _w 149000	14	41	-27	-42	15	[56]
95% ∟-lactide, <i>M</i> _w 185000	-2	37	-39	-42	3	[56]
100% L-lactide, quenched	-3	37	-40	-42	2	[56]
100% L-lactide, cooled	9	49	-40	-42	2	[247]
100% L-lactide, annealed	12	53	-41	-42	1	[56]
crystallined PLA	-0.1	n/a	n/a	-42		[247]
88% ∟-lactide	5	n/a	n/a	-42		[247]
88% L-lactide	31.4	39.2				[21]
PLA-graft			~-44			[245]
PLA at 1–49% RH	22.1±55.6°	97.5±19.7°	−71.6±5.5°	-42	~-30 ^d	This review
PLA at 50–79% RH	10.7±21.9℃	67.2±21.1°	-66.9±9.9°	-42	~-25 ^d	This review
PLA at 80–100% RH	−5.3±11.2°	70.6±19.6 ^c	-44.5±6.5°	-42	~-3 ^d	This review

Table 2-7 Activation energy of permeation (E_P), activation energy of diffusion (E_D), heat of sorption (ΔH_S), heat of condensation (ΔH_c), and heat of melting (ΔH_M) for H₂O.

^a Value reported from [148].
^b Values estimated from Eq. 26.

^c Average values of experimental data reviewed in this article and their standard deviations.

^d Values estimated from experimental data reviewed in this article.

Effect of relative humidity: While polar materials generally have high affinity to water, PLA, being quite polar due to its ester groups, does not show specific trends in P_{H_2O} with respect to RH (Figure 2-23). Fukuzumi et al. [175] determined P_{H_2O} at 10–40 °C, 20–80% RH and 23 °C, 30–90% RH conditions, respectively. They found that P_{H_2O} increased when RH increased. Siparsky et al. [56] estimated the P_{H_2O} values of several PLA samples at 50 °C, at 50% RH and 90% RH, but the trends were inconsistent. Auras et al. [63] reported that P_{H_2O} values at 40–90% RH did not change significantly.

<u>Effect of crystallinity and L:D ratio</u>: Results reported in the literature on the effect of PLA crystallinity on P_{H20} have been inconsistent. Some authors [248,254,269] found that P_{H_20} of PLA films decreased as X_c increased from 0 to 30% and leveled off when X_c was higher than 30%, while one study reported no significant change in P_{H_20} at low X_c , but a rapid decrease when X_c reached 39% [277]. A number of researchers observed an increase in P_{H_20} as X_c increased [13,56,63], and yet another study reported that crystallinity had no effect on P_{H20} in biaxially drawn PLA films [243]. These variations may be due to different processing methods or the existence of more than one amorphous phase in PLA. Further details of these studies are discussed below.

Siparsky et al. [56] observed a reduction in P_{H_2O} when X_c of semicrystalline PLA samples increased. However, when PLA samples were completely amorphous, a change in L:D ratio did not produce a trend for P_{H_2O} . Auras et al. [63] studied barrier properties of PLA films at different temperatures (10, 20, 30 and 38 °C) and different L-lactide contents. The authors found that higher L-lactide contents resulted in PLA films
with higher X_c and films with 98% L (40% X_c) had approximately 5% higher P_{H_2O} than films with 94% L (25% X_c) at 10 and 20 °C, and 2.5% higher at 30 and 38 °C. On the contrary, Shogren et al. [247] reported a decrease in P_{H_2O} when X_c increased from 0 to 66% at 6, 25 and 49 °C, and Duan and Thomas [254] found a monotonic reduction of P_{H_2O} from 0 to 50% X_c at 38 °C. At 25 °C, Tsuji et al. [248] reported a reduction in P_{H_2O} when X_c increased from 0 to 30%; however, P_{H_2O} remained constant above 30% X_c . These different findings of P_{H_2O} as a function of crystallinity may be explained on the basis of the presence of the three phases (CF, MAF and RAF) in the tested PLA films.

The effects of M_w , D-lactide, and X_c were studied by Tsuji et al. [248,269]. They found that changes in M_w of PLA films in the range of $9 \times 10^4 - 5 \times 10^5$ g.mol⁻¹ and Dlactide contents in the range of 0–50% did not have significant effects on P_{H_2O} . Siparsky et al. [56] also evaluated the effect of L:D-lactide ratio and did not find a trend. Tsuji and Tsuruno [269] examined the effect of crystallinity on P_{H_2O} at 25 °C, 90% RH of PLA films with different X_c . Their films were synthesized by ring-opening polymerization of Llactide (PLLA) and D-lactide (PDLA), as well as PLLA/PDLA blend films. For all films, P_{H_2O} decreased when X_c increased. P_{H_2O} of PLLA/PDLA blend films was 14–23% lower than pure PLLA and PDLA in X_c range of 0–30%. Amorphous PLLA/PDLA blend films had lower P_{H_2O} than pure PLLA and PDLA. Also, they found that P_{H_2O} was reduced by blending PLLA with PDLA even when the films were amorphous. This study found a dependence of P_{H_2O} on X_c for blend films within a range of 0–30% X_c , but not with X_c above 30%. P_{H_2O} of pure PLLA, PDLA, and blends decreased rapidly with increasing X_c in the range of 0–30% and then slowly between 30 and 100%. They attributed this change to the existence of the restricted amorphous regions at high X_c . Their concept of the restricted amorphous region is similar to the RAF in the three-phase model; however, they proposed that at high X_c the amorphous regions would be composed of solely restricted amorphous regions while at low X_c a small amount of free amorphous regions would coexist.

Mathematical models also have been applied to crystallinity results. Duan and Thomas [254] studied the permeability of PLA films with 0–50% X_c . The plot of P versus X_c showed a good fit to a linear trend line with negative slope. However, the trend line predicted zero permeability when crystallinity reached about 78%, which seemed unlikely (i.e., a polymer with less than 100% X_c is unlikely to be totally impermeable). They claimed that this phenomenon could be due to the presence of RAF at high X_c . The same authors [254] used the tortuous path model to predict that permeability reaches 0 at 100% X_c , and they claimed that this model provided the best explanation of the effect of crystallinity on P_{H_2O} in PLA.

Sansone et al. [172] studied the effect of high-pressure pasteurization on permeability of PLA flexible films. They found that PLA films pasteurized at 700 MPa had slightly lower P_{H_2O} than untreated PLA films at different temperatures (25 and 30 °C) and RH (30, 50 and 90%), while both films had similar X_c (approximately 25%). The reduction in P_{H_2O} was attributed to a decrease in water solubility due to structural changes in pasteurized films. Early studies conducted by Siparsky et al. [56] showed that PLA films after quenching (11% X_c) and after annealing (46% X_c) had different P_{H_2O} values. At 30, 40 and 50 °C, 50 and 90 % RH, quenched films had approximately 50% lower P_{H_2O} than annealed films. The effect of annealing on P_{H_2O} was also studied by

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others [147,254,272,277] and the results showed a monotonic decrease of P_{H_2O} as X_c decreased.

Delpouve et al. [243] studied water barrier of PLA films drawn by different drawing modes resulting in different X_c . The authors reported no effect of crystallinity on the P_{H_2O} . However, the macromolecular reorganization caused by the drawing process increased the tortuous path for water diffusivity, resulting in enhanced barrier.

2.7.2 Diffusion

Figure 2-24 shows Arrhenius plot of the *D* values of H₂O (D_{H_2O}) [56,89,222,278,279], with reported values of 2.4×10⁻¹⁵ to 6.6×10⁻¹¹ m².s⁻¹. Overall results show that D_{H_2O} increases as temperature increases. Due to large dispersion of the data, the effects of RH are not clear. However, a study of water diffusion in PLA [21] reported no effect of RH on D_{H_2O} . Results of D_{H_2O} reported by Gulati [89] are three orders of magnitude lower than results from other authors which may be attributed to the film thickness inconsistency, the possibility of defects in the films, and the method of measurement. Diffusion behavior of water in PLA films is non-Fickian [21,73]. Davis et al. [21] suggested that the initial water uptake is diffusion-driven by concentration gradient, while the later stage is controlled by stress relaxation or swelling due to the non-equilibrium state of PLA (glassy state).



Figure 2-24 Arrhenius plot of water vapor diffusion coefficients (D_{H_2O}) of PLA between 10 and 50 °C grouped by different relative humidity (RH) ranges. Each dashed line is from linear regression of the data in each RH range group. References: 1–49% RH = [21], \checkmark [89], \times [278]. 50–79% RH \circ [56], * [21], \triangle [89]. 80–100% RH \diamond [56], \triangleright [21], \Box [279], \triangleleft [89], + [222].

<u>Effect of temperature</u>: Generally, D_{H_2O} values increase with increasing temperature.

Gulati [89] found that D_{H_2O} increased by approximately 59% when temperature

increased from 10 to 40 °C at 20% RH. However, at 40% RH no significant change in

 D_{H_2O} was found. When PLA was exposed to 60 and 80% RH, D_{H_2O} decreased by

approximately 40% when temperature increased from 10 to 40 °C. The author attributed

inconsistencies in the results to the variability in the film thickness and the possibility of

structural defects in the films. Siparsky et al. [56] found that D_{H_20} decreased with increasing temperature. Activation energies obtained were in a range from 24 to 62 kJ.mol⁻¹ as shown in Table 2-7. They found a large variation from linearity in Arrhenius plots for PLA with 100% L-lactide between 40 and 50 °C compared to 20 and 40 °C. The authors attributed this variation to cluster formation. High condensation of water at lower temperatures increases the size and number of water formed clusters. Mobilization of water during diffusion is thus hampered at the lower temperatures. The average D_{H_20} values measured at 25, 35 and 45 °C reported by Davis et al. [21] also increased with increasing temperature.

Effect of relative humidity: With respect to RH, overall data do not show a specific trend. When Gulati [89] studied the barrier properties of PLA films, no significant change in D_{H_2O} values was found in the RH range of 20–80% at 10, 23 and 40 °C. Siparsky et al. [56] reported higher D_{H_2O} values at 90% RH than at 50% RH for PLA films with different L:D ratios at 50 °C. Davis et al. [21] reported that while D_{H_2O} varied with temperature, the values did not vary with RH in the range of 0–85% RH, which could be attributed to the low solubility of water in PLA.

Effect of crystallinity and L:D ratio: The effect of L-lactide was studied by Siparsky et al. [56]. The authors found that PLA films with 70% L had higher D_{H_2O} and lower E_{D,H_2O} values than those with 50 and 90% L. Drieskens et al. [147] reported a reduction of D_{H_2O} as crystallinity increased. However, D_{H_2O} was not independently measured, but rather was estimated from Eq. 11. When PLA films were compression molded, Siparsky et al.

[56] obtained quenched and annealed films with X_c of 11% and 46%, respectively. The values of D_{H_2O} calculated were approximately 50% higher when PLA was annealed. Drieskens et al. [147] reported that D_{H_2O} of PLA (96% L) annealed at 125 °C was higher than at 100 °C. Samples annealed at higher temperature for the same amount of time have higher X_c . The presence of higher RAF in samples with higher X_c could be responsible for this result.

2.7.3 Solubility

Figure 2-25 shows Arrhenius plots of the *S* values for H₂O (S_{H_2O}) [56,89,193,222,228,231]. Values of S_{H_2O} reported are 4.8×10^{-4} to 1.1×10^{-1} kg.m⁻³.Pa⁻¹. The values of S_{H_2O} decrease as temperature increases. The regression lines for different groups of RH shows higher S_{H_2O} at lower RH (1– 49%) which is counterintuitive, since the water sorption isotherms showed increasing sorbed water at higher water activities [280]. This may be attributed to inconsistency in film thickness and possible film defects, as reported by Gulati [89].



Figure 2-25 Arrhenius plot of water vapor solubility coefficients (S_{H_2O}) of PLA between 10 and 50 °C grouped by different relative humidity (RH) ranges. Each dashed line is from linear regression of the data in each RH range group. References: 1–49% RH \checkmark [89]. 50–79% RH \triangleright [56], \circ [89]. 80–100% RH \diamond [56], \Box [222], + [89].

<u>Effect of temperature</u>: Overall, S_{H_2O} decreased with increasing temperature, which

agrees with reported results [56,89] as shown in Figure 2-25.

Effect of relative humidity: A study by Gulati [89] showed that when RH increased from

20 to 80%, S_{H₂O} decreased 72, 33 and 54% at 10, 23 and 40 °C, respectively. Siparsky

et al. [56] showed that S_{H_2O} was relatively constant at intermediate temperatures

between 20 and 50 °C regardless of X_{c} , even for samples with a high amount of L-

lactide (50 and 70%). They attributed these results to the water cluster formation and

defined clustering in a polymer such as PLA as the ordered structure of a body of water within the polymer, which is stabilized by hydrogen bonding between the water molecules. The clustering does not necessarily affect the degree of crystallinity, but it affects the opacity of the film. Davis et al. [280,281] reported non-equilibrium sorption of water in PLA. They found that at water activities (a_w) less than 0.65 water is mostly present as dimers in PLA, but when a_w is higher than 0.65 a large hydrogen-bonded water cluster formation was observed. Furthermore, they reported that the water sorption and water-induced PLA relaxation in amorphous PLA (4032D) and in PLA homopolymer are taking place at the same time.

<u>Effect of crystallinity and L:D ratio</u>: Amorphous PLA at 20 °C showed smaller S_{H_2O} than semicrystalline PLA [245]. These results can be attributed to higher ΔH_S of the semicrystalline PLA.

2.7.4 Effect of modification

Different modifications have been performed on PLA to improve its properties. Figure 2-26 shows the percentage (%) of change in P_{H_20} when PLA is modified by the incorporation of additives, nanoparticles or blends of PLA with other polymers. The work by Duan et al. [272] showed the highest reduction in P_{H_20} with -46% change in P_{H_20} for nanocomposite of PLA 98% L and Cloisite[®] 30B. Generally, a decrease in P_{H_20} was observed with the incorporation of nanoparticles [150,272]. However, Katiyar et al. [214] reported that the addition of LDH-C₁₂ did not improve PLA barrier against the permeation of water vapor. Higher P_{H_20} for PLA melt processed with LDH-C₁₂ could be

due to water in LDH-C₁₂ causing PLA degradation, or the Mg-Al in LDH-C₁₂ catalyzing the degradation. When additives were present in the PLA matrix, P_{H_2O} increased [56,163]. Courgneau et al. [163] found that the addition of PEG resulted in approximately a 470% increase in P_{H_2O} compared with neat PLA. In this case, the presence of PEG could promote sorption of water due to the presence of hydrophilic groups providing hydrogen bonding between water and the ether group of PEG, leading to high S_{H_2O} and P_{H_2O} values [56].



Figure 2-26 % P_{H_2O} change for PLA films and different modifications. The numbers on top of the bars are P_{H_2O} (10⁻¹⁶ kg.m.m⁻².s⁻¹.Pa⁻¹) of neat PLA used in the corresponding experiments. (+) change means increasing P_{H_2O} (worse barrier) and (-) change means reduction of P_{H_2O} (better barrier). References: a [272], b [272], c [214], d [56], e [182], f [163], g [262]. Abbreviations: C30B = Cloisite® 30B, LDH = Mg-Al layered double hydroxide, PEG = poly(ethylene glycol), o-LA = lactic acid oligomer, ATBC = acetyl tributyl citrate, PCL = polycaprolactone.

2.7.5 Data gaps and recommendations

As previously described for gases, crystallization of PLA can produce CF and RAF. Due to the de-densification of the amorphous region present in the RAF, studies that properly measure RAF, which are currently lacking, should be conducted. Studies in this area could help to elucidate the variation of *P*, *D*, and *S* with CF, RAF and MAF. Large variations of these values have been reported, and most of the inconsistencies may be attributed to the lack of assessment of the RAF. A comprehensive understanding of the effect of RH on mass transfer of water vapor through PLA is missing since data

presented in this review do not show any trend of P_{H_2O} with RH. Additionally, a few authors reported clustering of water in PLA. Additional studies should be conducted to fully quantify clustering of water as a function of temperature.

2.8 Mass transfer of organic vapors

Barrier properties of PLA to different organic vapors, such as ethylene (C₂H₄), benzaldehyde, ethyl acetate, eucalyptol, and estragole have been conducted. In general, *P* and *D* increase with temperature, but *S* decreases when temperature increases. It has been reported that the higher the X_c of PLA the lower the *P*, *D*, and *S* to some organic vapors. Interesting results were found in the study of PLA barrier properties to some organic vapors, such as methanol, ethanol and ethyl acetate. The presence of these compounds induces crystallization in PLA in which *P* and *D* decrease as X_c increases over time. Specific details of the studies and findings of each parameter are discussed below.

2.8.1 Permeability

Figure 2-27 shows a plot of *P* of different organic compounds grouped by similar test temperatures versus M_w at 0% RH. A general linear reduction of *P* is observed as M_w increased, as expected. However, it is difficult to correlate *P* with M_w since different compounds were not measured at the same temperature, and the functional groups are different. We can observe a large variation of *P* for the same compound as a function of temperature.

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Figure 2-27 *P* of different organic compounds grouped by similar test temperatures versus M_w at 0% RH. References: methanol [190], ethanol [190], acetaldehyde [184], ethyl acetate [137,159], d-limonene [282], estragole [283], eucalyptol [283].

<u>Effect of temperature</u>: Figure 2-28 shows *P* of PLA exposed to different organic vapors at different temperatures. Different authors have studied the effects of temperature on *P* of different organic vapors, such as eucalyptol, estragole, and ethyl acetate, where *P* increases with temperature. Eucalyptol and estragole were studied by Leelaphiwat et al. [283]. They reported *P* of eucalyptol and estragole increased 2.2 times and 1,258 times, respectively, from 15 to 25 °C. Auras et al. [148] observed that *P* of ethyl acetate depended on temperature where *P* increased with temperature from 30 to 45 °C.



Figure 2-28 Arrhenius plot of permeability coefficients (*P*) of organic compounds in PLA at 0% RH. References: d-limonene [282], ethyl acetate [137,159], estragole [283], eucalyptol [283], ethanol [190], methanol [190], acetaldehyde [184], trans-2-hexanal [184].

<u>Effect of crystallinity and L:D ratio</u>: *P* of several organic vapors have been investigated in PLA films with different X_c and L:D lactide ratios. In general, the higher the X_c of PLA the lower the *P*. Important studies have been carried out where organic vapors induced the crystallization of the tested PLA. Duan et al. [272] studied permeability of methanol and ethanol at 0% RH, at 25, 35 and 45 °C for up to 1440 min. *P* values of PLA exposed to methanol at 25 °C and ethanol at 25 and 35 °C were constant with increasing exposure time. However, for PLA exposed to methanol at 35 and 45 °C, *P* values decreased with increasing exposure time. This was attributed to the presence of ethanol and methanol that induced crystallization in PLA, thereby decreasing the *P* as

 X_c increased. Amorphous films exposed to methanol for 1440 min at 25, 35 and 45 °C increased X_c to 2.8, 13.1 and 24.7%, respectively. In the case of ethanol, PLA exposed at 25, 35 and 45 °C increased X_c to 1.2, 3.5 and 26.7%, respectively.

2.8.2 Diffusion

Figure 2-29 shows *D* of organic compounds grouped by similar test temperature versus their molecular volumes (*V*). As *V* increases, we should observe a reduction of *D* since larger molecules diffuse more slowly. Figure 2-29 shows that there is a reduction in *D* with respect to *V* at the same temperature.



Figure 2-29 *D* of organic compounds grouped by similar test temperature versus their molecular volumes (*V*). References: ethyl acetate [137,159], ethyl butanoate [160], ethyl hexanoate [284], d-limonene [282], estragole [283], eucalyptol [283].

<u>Effect of temperature</u>: Figure 2-30 shows *D* of organic compounds in PLA (in logarithmic scale) as a function of reciprocal of absolute temperature. Leelaphiwat et al. [283] found that *D* of eucalyptol increased with increasing temperature (15 and 25 °C) almost 4 times, and approximately 14 times for estragole, with eucalyptol having higher *D* values. For ethyl acetate, *D* also increased with increasing temperature [13].



Figure 2-30 Arrhenius plot of diffusion coefficients (*D*) of organic compounds in PLA at 0% RH. References: d-limonene [282], ethyl acetate [137,160,168,284], ethyl butanoate [160], ethyl hexanoate [160,284], estragole [283], eucalyptol [283], linalool [283].

<u>Effect of crystallinity and L:D ratio</u>: Ethyl acetate is one of the organic vapors being studied that induces crystallization in PLA. Diffusion of ethyl acetate at 25 °C was investigated by Courgneau et al. [168] in PLA with different treatments: PLA non-annealed (3% X_c) and PLA with recrystallization temperature 120 °C (43% X_c). After contact with ethyl acetate for 2 weeks, the crystallinity increased to 26 and 44% for PLA non-annealed and PLA recrystallized at 120 °C, respectively. *D* was lower for PLA with high X_c , with values of 2.40×10⁻¹⁷ for 3% X_c and 1.60×10⁻¹⁷ kg.m.m⁻².s⁻¹.Pa⁻¹ for 43% X_c .

2.8.3 Solubility

Figure 2-31 shows *S* of organic compounds in PLA (in logarithmic scale) as a function of reciprocal of absolute temperature at 0% RH. Values are largely reported at 25 °C. The highest *S* among reported data is from estragole at 6.82 kg.m⁻³.Pa⁻¹ and the lowest *S* from ethyl acetate at 4.72×10^{-7} kg.m⁻³.Pa⁻¹.



Figure 2-31 Arrhenius plot of solubility coefficients (*S*) of organic compounds in PLA at 0% RH. References: 2-nonanone [285], benzaldehyde [285], ethylene [228], d-limonene [282], ethyl acetate [137,159,168,284,285], ethyl butanoate [285], ethyl hexanoate [284,285], estragole [283], eucalyptol [283].

<u>Effect of temperature</u>: Auras et al. [148] found that *S* of ethyl acetate in PLA decreased as temperature increased from 30 to 40 °C. The same tendency for *S* of ethyl acetate was found by Oliveira et al. [228] with PLA cooled down from melt (10% *X_c*) and PLA

annealed at temperature slightly above T_g (20% X_c). When exposed to C₂H₄, S of PLA from melt decreased 43% from 10 to 40 °C and S of annealed PLA decreased by 50% [228].

Effect of crystallinity and L:D ratio: Colomines et al. [159] studied S of ethyl acetate in different PLA films: extruded, quenched, recrystallized and commercial PLA Biophan with X_c of 2, 6, 39 and 19%, respectively. They found that ethyl acetate induces crystallization at 0.5 and 0.7 vapor activities, resulting in lower S value. The authors also found that the higher the X_c , the lower the S values. Different processing treatments of PLA affect crystallinity of the materials and thus, S of the organic vapor. Recrystallized samples tend to absorb a small quantity because the sorption occurs only in the amorphous phase of the polymer; however, no characterization of RAF was reported in these studies. Solubility of ethyl acetate in PLA has been studied by different authors [159,168,284]. Courgneau et al. [168] studied the solubility in different PLA treatments: PLA non-annealed (3% X_c) and PLA with a recrystallization temperature of 90 (36% X_c) and 120 °C (43% X_c). They found that the higher the X_c the lower the S where S decreased 7.6% from 0 to 36% X_c. Furthermore, the S of ethyl acetate was investigated by Domenek et al. [284] along with S of ethyl hexanoate in commercial PLA Biophan, extruded, and cast film PLA. The authors found that S values were the same for different types of films. However, S of ethyl hexanoate was lower than S of ethyl acetate due to the hydrophobicity of ethyl hexanoate. Oliveira et al. [228] studied S of C_2H_4 in PLA cooled down from the melt (10% X_c) and PLA annealed at temperature slightly above T_g (20% X_c). At 30 °C, S of C₂H₄ in annealed PLA was approximately 15% larger

than in PLA cooled down from melt, which may be explained by different amounts of FV due to different *X*_c. In addition to *S* of vapors, Tsuji and Sumida [286] studied the effects of organic solvents on the degree of swelling (DS) and other physical properties, based on solubility parameters of PLA and the solvents. The authors found that the physical properties of PLA films could be modified due to swelling induced by the solvents with different solubility parameter values, as well as the DS.

2.8.4 Effect of modification

Several studies have reported the effect of modification of PLA on organic vapor barrier properties. Table 2-8 shows the incorporation of different additives and the effect on *D* and *S* of ethyl acetate, ethyl butyrate, and ethyl hexanoate. In all cases, the values increased with respect to neat PLA. The addition of talc/ATBC appears to significantly affect both *D* and *S* of ethyl acetate, resulting in 417000% and 11100% increases, respectively.

Parameter	Туре	Material	Modification	%Change	References
				× 10 ²	
D	Ethyl	PLA/talc/ATBC	Additive	4170	[287]
	acetate	non-annealed			
D	Ethyl	Plasticized PDLLA	Additive	39.2	[160]
	butyrate	(200µm)			
D	Ethyl	Plasticized PDLLA	Additive	20.8	[160]
	hexanoate	(200µm)			
S	Ethyl	PLA/talc/ATBC	Additive	111	[287]
	acetate	non-annealed			

Table 2-8 Mass transfer parameters of organic compounds for modified PLA films, at 25 °C, 0% RH.

2.8.5 Data gaps and recommendations

Overall very few *P*, *D*, and *S* values for organic compounds have been reported for PLA. *P* and *D* seem to be reduced as M_w and *V* are increased. Systematic studies of organic family compounds such as n-alkenes, n-alcohols, and esters have not yet been reported. Studies of the effect of RH on *P*, *D*, and *S* of organic vapors are also lacking. Furthermore, plasticization effects of organic vapors on PLA are not well understood. The effect of modifications is not fully investigated. So, increasing effort should be targeted on measuring these parameters.

2.9 Comparisons of barrier properties of PLA to common commercial films

Table 2-9 shows *P* of PLA and other common commercial films at 25 °C and Figure 2-32 illustrates comparisons of these values. PLA shows moderate values of *P* for gases, higher than PET but mostly lower than PE, PS, and PP. However, PLA has very high P_{H_20} when compared with other polymers. It is apparent that PLA by itself is not suitable for applications that require high barrier against gases and water vapor. However, as mentioned before, there are various methods to enhance PLA barrier properties, such as adjusting the L- and D-lactide ratios in the manufacturing process, coextruding with a high barrier polymer, or adding clay/nanoclay. Thus, with an advantage of being a bio-based and compostable polymer, PLA can be a candidate for applications that require moderate to high barrier, but may require some modifications.

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	$P_{0_2} \times 10^{-20}$	$P_{CO_2} \times 10^{-20}$	$P_{N_2} \times 10^{-20}$	$P_{H_2O} \times 10^{-16}$
PLA ^a	315±150	2811±842	32.2±2.8	161±41
LDPE	3100	18600	914	5.51
HDPE	424	538	137	2.02
PP	1790	10500	286	3.12
PS, biaxially oriented	2860	15500	742	57.8–67.5
PAN (Barex™)	5.87	23.6	n/a	39.5
PVAL	0.07–9.46	18.2	0.13 ^b	n/a
EVOH, 32% ethylene	0.09	0.36	0.005	n/a
EVOH, 44% ethylene	0.41	3.14	0.04	n/a
PVDC (Saran™)	3.59	31.4	0.56	0.56
PTFE (Teflon™)	4570	149000	1260	0.49
PVC, unplasticized	49	247	11.1	16.5
PET, 40% <i>X_c</i>	35.9	179	55.7	7.8
PET, amorphous	62	449	n/a	n/a
PC (Lexan)	1480	1170	271	83.5
Nylon 6	31	171	6.57	n/a
Cellophane ^c	9.46	105	7	n/a

Table 2-9 Permeability coefficients (*P*) of PLA in kg.m.m⁻².s⁻¹.Pa⁻¹ to selective gases and vapors and a comparison with other commercial available polymers [81]. All *P* values were measured at 25 °C unless indicated otherwise.

n/a: not available, ^a data from this review, reported as average value ± standard deviation, ^b measured at 14 °C, ^c measured at 76% RH.

Polymer name abbreviations: PLA = poly(lactic acid), LDPE = low density polyethylene, HDPE = high density polyethylene, PP = polypropylene, PS = polystyrene, PAN = polyacrylonitrile, PVAL = poly(vinyl alcohol), EVOH = ethylene vinyl alcohol, PVDC = poly(vinylidene chloride), PTFE = polytetrafluoroethylene, PVC = poly(vinyl chloride), PET = poly(ethylene terephthalate), PC = polycarbonate.



Figure 2-32 Comparisons of *P* of different gases and vapors at 25 °C in various polymers. (Data adapted from [81] and measured results in this review.)

Polymer name abbreviations: PLA = poly(lactic acid), LDPE = low density polyethylene, HDPE = high density polyethylene, PP = polypropylene, PS = polystyrene, PET = poly(ethylene terephthalate), aPET = amorphous PET.

2.10 Migration of chemical compounds

Migration is a phenomenon resulting from the diffusion and dissolution of low molecular mass compounds (i.e., migrants) initially present in a polymer that are released into liquid media. It is a very crucial process for development of release compounds for medical applications and active packaging. Similar to mass transfer mechanism introduced in Section 2.4.1, diffusion of a migrant occurs through the amorphous regions of the polymer towards the interface. When the mass transfer reaches equilibrium, the partition coefficient of the migrants between polymer *p* and liquid *f*, $K_{\rho,f}$, determines the equilibrium concentration and distribution in the two phases [288–290].

Different studies on migration of chemical compounds from PLA have been performed. These studies are focused either on medical applications for drug release or on food packaging applications. In medical applications, PLA has been used as a drug release system due to its biocompatibility, its degradation into non-toxic monomers, and because the migration of chemical compounds can be controlled by changing the molecular weight and monomer ratio of PLA [291–293]. In food packaging, researchers have focused on positive migration studies, for example, adding antioxidants/antimicrobials that can migrate from a PLA matrix to food products to prolong their shelf life [49,240,294–297].

Migration phenomena of chemical compounds may be expressed mathematically. Table 2-10 shows a list of mathematical models that have been applied to estimate the parameters that describe the migration of different compounds from PLA to different media at different temperatures. Generally, these models are based on the Higuchi model and Fick's law. The Higuchi model is based on the release of high and

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low water-soluble drugs incorporated in semi-solid and/or solid matrices [298–305]. Different models based on Fick's law have been applied to migration of chemical compounds from PLA that describe: 1) migration into infinite volume of solution and negligible external mass transfer coefficient [260,294,306–312]; 2) migration into infinite volume of solution and non-negligible external mass transfer coefficient [309]; and 3) migration into finite volume of solution and negligible external mass transfer coefficient [195,308–310,313]. Other models are based on concepts of dissolution-diffusion or burst effect [314,315].

Table 2-10 Studies reporting kinetic migration parameters using mathematical models for PLA incorporated with different chemical compounds

Compound	Application	Medium	T, ℃	Mathematical models	Model Type	Parameters estimated	Ref.
Vancomycin	Drug release	Phosphate buffer, pH 7.4	37	$\frac{Q}{Q_0} = k_h t^{1/2}$	Higuchi	k	[300]
Acetaminophen	Drug release	Phosphate buffer, pH 7.4	37	$\frac{Q}{Q_0} = k_h t^{1/2}$ $\log\left(\frac{Q_1}{Q_0}\right) = \frac{k_1 t}{2.303}$	Higuchi	k	[301]
Nonionic hydrophobic dye	Agrichemical	Water and phosphate buffer, pH 7.4	Room (~23)	$f(t) = B_1 t^{1/2}$	Higuchi	f(t)	[302]
Lactic acid/lactide	Food- contact	8% ethanol	26, 43	$D = \frac{slope^2\pi}{(2\rho C)^2}$	n/a	D	[316]

Compound	Application Medium		T. ℃	Mathematical models	Model	Parameters	Ref.
compound	ripplication	modium	., -		Туре	estimated	i ton
Ascorbyl palmitate, α-tocopherol, BHA, BHT and	Food- contact	10, 50 and 95% ethanol	20, 40	$\frac{M_t}{M_{\infty}} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)} exp\left[-\frac{(2n+1)^2 \pi^2}{L^2} Dt\right]$	Fick's law	D and $K_{p,f}$	[306]
TBHQ				$\frac{M_t}{M_{\infty}} = 4(Dt/4L^2\pi)^{1/2}$			
BHA, BHT, PG and TBHQ	Food- contact	10, 50 and 95% ethanol	20, 40	$\frac{M_t}{M_{\infty}} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)} exp\left[-\frac{(2n+1)^2 \pi^2}{L^2} Dt\right]$	Fick's law	D and $K_{p,f}$	[260]
				$\frac{M_t}{M_{\infty}} = 4(Dt/4L^2\pi)^{1/2}$			
4-Nitroanisole	Drug release	Phosphate buffer, pH	37	$\frac{M_t}{M_{\infty}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} exp\left(-\frac{Dn^2\pi^2 t}{R_s^2}\right) u$	Fick's law	D	[307]
		7.4		$\frac{M_t}{M_{\infty}} = 6 \left(\frac{D_1 t}{\pi R_s^2} \right)$			

Compound	Application	Medium	T, °C	Mathematical models	Model Type	Parameters estimated	Ref.
Lidocaine	Drug release	Phosphate buffer, pH 7.4	37	$\frac{M_t}{M_{\infty}} = 6 \left(\frac{Dt}{r^2}\right)^{0.5} - 3\frac{Dt}{r^2}$	Fick's law	D and $K_{p,f}$	[317]
Nimesulide	Drug release	Phosphate buffer, pH 7.4	37	$Q_t = Q_0 + k_0 t$ $Q_1 = k_h t^{1/2}$ $(3/2) [1 - (1 - Md/Mt)^{2/3}] - (Md/Mt) = kt$	Higuchi	k	[304]
Nifedipine	Drug release	Phosphate buffer	37	$\frac{\partial C_L(r,t)}{\partial t} = D\left(\frac{\partial^2 C_L(r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial C_L(r,t)}{\partial r}\right) + k sgn(C_S(r,t)) \times (C_{sat} - C_L(r,t))$	Dissolution- diffusion	D and k	[314]
Lidocaine	Drug release	Phosphate buffer, pH 7.4	37	$\frac{c_1}{c_{1\infty}} 1 - \sum_{n=1}^{\infty} \frac{6\alpha(1+\alpha)}{9+9\alpha+(\alpha q_n)^2} exp\left(-\frac{Dq_n^2 t}{R^2}\right)$ $c_1 = \frac{c_0}{K_p(\alpha+1)} \left[1 - exp\left(-\frac{\alpha+1}{\alpha}kt\right)\right]$	Dissolution- diffusion	D, $K_{dissolution}$ and $K_{p,f}$	[318]
Progesterone	Drug release	Water	37	$\frac{M_t}{M_{\infty}} = (A^2 + Bt)^{1/2} - A$	n/a	D	[319]

Compound	Application	Medium	T, ℃	Mathematical models	Model Type	Parameters estimated	Ref.
Silver	Antimicrobial	Water, 3% acetic acid, 95% ethanol	4, 20	$\frac{m(t)}{c_P A \lambda} = 4 \sqrt{\frac{Dt}{\pi \lambda^2}}$	n/a	D	[320]
Thyme oil		water bath	room	$m_{i,2}(t) = m_{i,2}^{eq} + (m_{i,2}^0 - m_{i,2}^{eq}) \times e^{Dt/\frac{r_P(r_P^3 - r_c^3)}{3(r_P^2 - r_c^2)} - \frac{r_P^2 - r_c^2}{4} - \varepsilon_1 \frac{r_P^3 - r_c^3}{(r_P - r_c)}}$	Fick's law	D	[321]
Catechin and epicatechin	Food- contact	50 and 95% ethanol	20, 30, 40, 50	$\frac{M_t}{M_{\infty}} = 1 - \sum_{n=0}^{\infty} \frac{2\alpha(1-\alpha)}{1+\alpha+\alpha^2 q_n^2} exp\left(-\frac{Dq_n^2 t}{l^2}\right)$ $\frac{M_t}{M_{\infty}} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} exp\left(-\frac{D(2m+1)^2 \pi^2 t}{l^2}\right)$	Fick's law	D, $lpha$ and $K_{ ho,f}$	[308]
Propolis	Food- contact	water and ethanol	25	$\begin{split} \frac{M_t}{M_{\infty}} &= 1 - \frac{8}{\pi} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} exp\left(-\frac{(2n+1)^2}{4L^2} \pi^2 Dt\right) \\ \frac{M_t}{M_{\infty}} &= 1 - \sum_{n=1}^{\infty} \frac{2R^2}{\beta_n^2 (\beta_n^2 + R^2 + R)} exp\left(-\beta_n^2 \frac{Dt}{L^2}\right) \\ \frac{M_t}{M_{\infty}} &= 1 - \sum_{n=1}^{\infty} \frac{2\alpha (1-\alpha)}{1+\alpha + \alpha^2 q_n^2} exp\left(-\frac{Dq_n^2 t}{l^2}\right) \end{split}$	Fick's law	D, Bi, K _{external mass} transfer and K _{p,f}	[309]

Compound	Application	Medium	T, ℃	Mathematical models	Model Type	Parameters estimated	Ref.
α-tocopherol	Food- contact	ethanol	23, 33, 43	$\frac{M_t}{M_{\infty}} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1-\alpha)}{1+\alpha+\alpha^2 q_n^2} exp\left(-\frac{Dq_n^2 t}{l^2}\right)$ $\frac{M_t}{M_{\infty}} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} exp\left(-\frac{D(2m+1)^2 \pi^2 t}{l^2}\right)$	Fick's law	D, α and K _{p,f}	[310]
Resveratrol	Food- contact	ethanol	9, 23, 33, 43	$\frac{M_t}{M_{\infty}} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} exp\left(-\frac{D(2m+1)^2 \pi^2 t}{l^2}\right)$	Fick's law	D and $K_{p,f}$	[312]
ВНТ	Food- contact	ethanol	23, 31, 43	$\frac{M_t}{M_{\infty}} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1-\alpha)}{1+\alpha+\alpha^2 q_n^2} exp\left(-\frac{Dq_n^2 t}{l^2}\right)$ $\frac{M_t}{M_{\infty}} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} exp\left(-\frac{D(2m+1)^2 \pi^2 t}{l^2}\right)$	Fick's law	D, α and K _{p,f}	[195]
Astaxanthin	Food- contact	95% ethanol	30, 40	$\frac{M_t}{M_{\infty}} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1-\alpha)}{1+\alpha+\alpha^2 q_n^2} exp\left(-\frac{Dq_n^2 t}{l^2}\right)$	Fick's law	D, $lpha$ and $K_{ ho,f}$	[313]

Compound	Application	Medium	T, °C	Mathematical models	Model Type	Parameters estimated	Ref.
Epigallocatechin gallate	Food- contact	water	37	$\frac{MF,t}{Mfe} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} exp\left(-\frac{(2n+1)^2 \pi^2}{4d_p^2} Dt\right)$ $D = \frac{\pi}{4} \left(S_{F,\infty} d_p\right)^2$	Fick's law	D	[311]
Thymol	Food- contact	950 and 150 mL/L ethanol/water	30, 40, 50, 60, 65, 75, 83	$ln\left(1-\frac{m_t}{m_{\infty}}\right) = -k_1 t$ $v_0 = m_{\infty} k_1$ $\frac{m_t}{m_{\infty}} = 4\left(\frac{Dt}{\pi l^2}\right)^{1/2}$ $\frac{m_t}{m_{\infty}} = 1 - \left(\frac{8}{\pi^2}\right)exp\left(-\frac{\pi^2 Dt}{l^2}\right)$ $\frac{m_t}{m_{\infty}} = 1 - \frac{8}{\pi^2}\sum_{m=0}^{\infty}\frac{1}{(2m+1)^2}exp\left(-\frac{D(2m+1)^2\pi^2 t}{l^2}\right)$	Fick's law	<i>k, v</i> ₀and D	[294]
Silver	Food- contact	10% ethanol	40	$\frac{M_{F,t}}{M_{P.0}} = \frac{2}{L_p} \left(\frac{Dt}{\pi}\right)^{0.5}$	Fick's law	D	[252]

Compound	Application	Medium	T, ℃	Mathematical models	Model Type	Parameters estimated	Ref.
Oligonucleotides	Drug release	foetal calf serum, phosphate buffer pH 7.4, citrate phosphate pH 5.5	37	$M_{t} = (M_{0} - M_{b}) \left(1 - \sum_{n=0}^{\infty} \frac{8 \exp\left[\frac{-D(2n+1)^{2}\pi^{2}r^{2}}{h^{2}}\right]}{(2n+1)^{2}\pi^{2}} \right) + M_{b}$	Fick's law	D	[315]
Mitomycin C	Drug release	Phospate buffer, pH 7.4	37	$\frac{3}{2} \left[1 - (m_t/m_\infty)^{2/3} \right] - (m_t/m_\infty) = 3C_s D t/r_0^2 A$	Higuchi	D	[303]
Phenobarbitone	Drug release	Buffer pH 2	37	$Q = k_h t^{1/2}$	Higuchi	k	[305]
Allyl isothiocyanate	Food- contact	Head space, 0 and 75% RH	37	$C = C_e (1 - e^{-kt})$	n/a	k	[322]
Hydrocortisone	Drug release	Phospate buffer, pH 7.4	37	$1 \cdot 5 [1 - (1 - m_t/m_{\infty})^{2/3}] - (m_t/m_{\infty}) = Bt$ $B = 3C_s D/r_0^2 A$	n/a	B and D	[323]

Compound	Application	Medium	T, °C		Model	Parameters	Def
Compound	Application			Mathematical models	Туре	estimated	Rei.
				$J_{I} = \frac{D_{Thy}}{L/2} \cdot \left(C_{Thy}^{PLA}(x=0,t) - C_{Thy}^{PLA}(x=L/2,t) \right)$			
Thymol	Food-	10 and 95%	40		n/a	Dand K.	[300]
Thymon	contact	ethanol	-10	$J_{II} = k \cdot \left(C_{Thy}^{SS}(x = L/2, t) - C_{Thy}^{SS}(x = \infty, t) \right)$	n/a		[500]

n/a: Model type not specified

Table 2-11 shows the estimated values of *D* for chemical compounds from Table 2-10. Different media have been used in migration studies of PLA. For drug release systems, generally phosphate buffer solution (pH 7.4) at 37 °C is applied to simulate human body conditions. However, for food packaging applications, diverse simulants are used in contact with PLA. For instance, in accordance with the U.S. Food and Drug Administration (U.S. FDA) and the European Union Directives, 95% ethanol, 50% ethanol, and water are commonly used food simulants for fatty, alcoholic and watery liquid products, respectively [324,325].

Lactic acid/lactide 8% ethanol 26 0.00004 $[316]$ α -tocopherol 95% ethanol 20 0.20 α -tocopherol 95% ethanol 20 0.20 BHA 95% ethanol 20 0.321 BHA 50% ethanol 20 0.321 10% ethanol 20 0.321 10% ethanol 20 0.74 20 0.28 20 10% ethanol 20 0.074 20 2.28 20 20 0.16 20 BHT 95% ethanol 20 0.16 95% ethanol 20 0.612 $Propyl gallate$ 95% ethanol 20 0.0756 10% ethanol 20 0.816 95% BHA 10% ethanol 40 0.36 BHA 95% ethanol 20 0.00297 BHT 95% ethanol 20 0.27 $[260]$	Compound	Media	T, °C	<i>Dx</i> 10 ⁻¹⁴ , m ² .s ⁻¹	Reference
Loss contrainer 43 0.002 [919] a-locopherol 95% ethanol 40 14.90 20 0.20 0.20 BHA 95% ethanol 20 0.321 20 0.321 0.074 0.002 BHA 50% ethanol 20 0.074 20 0.074 0.074 0.074 20 2.28 0.0074 0.0584 20 0.16 0.0612 0.612 BHT 95% ethanol 20 0.612 95% ethanol 20 0.0756 0.00297 Propyl gallate 50% ethanol 40 0.312 Propyl gallate 95% ethanol 20 0.0756 10% ethanol 40 2.78 9.50 BHA 10% ethanol 20 0.0756 10% ethanol 40 2.78 9.50 BHA 50% ethanol 40 0.312 10% ethanol 40 0.27 [260] 20 <td>Lactic acid/lactide</td> <td>8% ethanol</td> <td>26</td> <td>0.00004</td> <td>[316]</td>	Lactic acid/lactide	8% ethanol	26	0.00004	[316]
α -tocopherol 95% ethanol 40 14.90 α -tocopherol 95% ethanol 20 0.20 BHA 95% ethanol 20 0.321 BHA 30% ethanol 20 0.074 10% ethanol 20 0.074 0 10% ethanol 20 0.074 0 10% ethanol 20 0.16 0 BHT 95% ethanol 20 0.16 BHT 95% ethanol 20 0.612 95% ethanol 20 0.612 0 95% ethanol 20 0.612 0 10% ethanol 20 0.0756 0 10% ethanol 20 0.816 0 10% ethanol 40 2.78 9 10% ethanol 40 0.816 9 BHA 95% ethanol 20 0.00297 BHT 95% ethanol 40 0.27 [260] BHT 95% ethanol 0		070 Ctrianor	43	0.002	[510]
No certained 20 0.20 20 0.20 Auge 40 43.10 20 0.321 20 0.321 20 0.074 20 0.074 20 0.074 20 0.228 20 2.28 20 2.28 20 0.16 20 0.16 20 0.16 20 0.10 20 0.10 20 0.10 20 0.10 20 0.10 20 0.612 20 0.612 20 0.612 20 0.612 20 0.612 20 0.612 20 0.816 20 0.816 20 0.271 20 0.0297 50% ethanol 40 0.27 20 0.271 20 0.2027	a-tocopherol	95% ethanol	40	14.90	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		5570 Cilianol	20	0.20	
BHA 20 0.321 BHA 30% ethanol 40 1.12 20 0.074 20 2.28 10% ethanol 20 2.28 20 2.28 20 2.28 BHT 95% ethanol 20 0.16 0.584 50% ethanol 20 0.16 0.584 50% ethanol 20 0.612 0.612 Propyl gallate 95% ethanol 40 39.00 95% ethanol 20 0.612 0.0756 10% ethanol 40 2.78 0.0756 10% ethanol 40 2.78 0.015 BHA 95% ethanol 20 0.816 BHA 95% ethanol 40 0.36 10% ethanol 40 0.19 1.60 BHA 95% ethanol 20 0.00237 60% ethanol 40 0.27 260 BHT 95% ethanol 20 0.27 20 0.27		95% ethanol	40	43.10	
BHA 50% ethanol 40 1.12 20 0.074 10% ethanol 40 2.28 20 2.28 20 0.16 50% ethanol 20 0.16 50% ethanol 20 0.16 50% ethanol 20 0.10 95% ethanol 20 0.10 95% ethanol 20 0.612 96% ethanol 20 0.0756 10% ethanol 20 0.0756 10% ethanol 20 0.816 95% ethanol 20 2.66 50% ethanol 40 59.90 20 0.00297 2.66 50% ethanol 40 0.19 95% ethanol 40 0.27 10% ethanol 20 0.00297 BHT 95% ethanol 20 0.27 10% ethanol 20 0.27 20 BHT 95% ethanol 20 0.27 20 0.27 <t< td=""><td></td><td>3370 ethanol</td><td>20</td><td>0.321</td><td></td></t<>		3370 ethanol	20	0.321	
Drive 30% ethanol 20 0.074 10% ethanol 40 2.28 20 2.28 Propyl gallate 95% ethanol 20 0.16 50% ethanol 20 0.16 0.584 20 0.10 0.584 0.074 Propyl gallate 95% ethanol 20 0.16 95% ethanol 20 0.612 0.612 95% ethanol 20 0.0756 0.0756 10% ethanol 20 0.816 0.019 BHA 95% ethanol 20 2.66 50% ethanol 40 0.36 10% ethanol 95% ethanol 20 0.612 10% ethanol BHA 95% ethanol 20 0.266 50% ethanol 40 0.19 10% ethanol 20 0.00297 BHT 95% ethanol 20 0.27 [260] [260] Propyl gallate 95% ethanol 20 0.27 [260] 20 0.	вни	50% otheral	40	1.12	
10% ethanol402.28202.2895% ethanol200.162050% ethanol0.584200.1000.1095% ethanol2000% ethanol2000% ethanol2000% ethanol2000% ethanol20200.61210% ethanol2010% ethanol2010% ethanol2010% ethanol2010% ethanol2010% ethanol40200.81650% ethanol40202.6650% ethanol4010% ethanol40002.6650% ethanol4010% ethanol0.1910% ethanol20200.0029760% ethanol20200.2795% ethanol20200.2795% ethanol20200.2795% ethanol20200.2795% ethanol202030.902030.9020% ethanol1.0220% ethanol2020% ethanol20 </td <td></td> <td>50 % ethanol</td> <td>20</td> <td>0.074</td> <td></td>		50 % ethanol	20	0.074	
10% ethanol 20 2.28 BHT 95% ethanol 20 0.16 50% ethanol 20 0.584 50% ethanol 20 0.10 Propyl gallate 95% ethanol 20 0.612 95% ethanol 20 0.612 0.00756 10% ethanol 20 0.0756 0.0756 10% ethanol 40 2.78 0.01756 10% ethanol 20 0.816 0.011 BHA 95% ethanol 20 2.666 50% ethanol 40 0.36 1.02 BHA 95% ethanol 40 0.36 10% ethanol 40 0.36 1.02 50% ethanol 40 0.27 [260] 60% ethanol 20 0.27 [260] 95% ethanol 20 0.27 [260] 60% ethanol 20 30.90 [260] 95% ethanol 20 30.90 [260] 20 30.90		10% otherol	40	2.28	
BHT 95% ethanol 40 31.20 [306] BHT 50% ethanol 20 0.16 [306] 50% ethanol 20 0.10 [306] Propyl gallate 95% ethanol 20 0.10 Propyl gallate 50% ethanol 20 0.612 10% ethanol 40 1.28 20 0.0756 10% ethanol 20 0.816 20 0.816 BHA 95% ethanol 20 2.666 20 0.0297 BHA 95% ethanol 40 2.410 20 0.0297 BHT 95% ethanol 40 0.27 [260] BHT 95% ethanol 20 0.277 [260] Propyl gallate 95% ethanol 20 30.90 [260] BHT 95% ethanol 20 30.90 [260] 20 30.90 Propyl gallate 50% ethanol 20 30.90 [260] 1.50			20	2.28	
BHT 20 0.16 [500] BHT 20 0.16 0.584 20 0.10 20 0.10 Propyl gallate 95% ethanol 20 0.612 Propyl gallate 60% ethanol 20 0.0756 10% ethanol 20 0.816 10% ethanol 20 0.816 60% ethanol 40 59.90 20 0.816 20 BHA 95% ethanol 40 0.36 60% ethanol 40 0.36 20 BHA 95% ethanol 40 0.27 BHT 95% ethanol 20 0.27 95% ethanol 20 0.27 [260] Propyl gallate 95% ethanol 20 0.27 20 0.27 [260] 20 30.90 Propyl gallate 95% ethanol 20 30.90 20 20 30.90 20 30.90 20 30.90 20	BHT	95% otherol	40	31.20	[306]
bin 40 0.584 20 0.10 Propyl gallate 95% ethanol 20 0.612 Propyl gallate 50% ethanol 20 0.612 10% ethanol 20 0.0756 10% ethanol 40 2.78 20 0.816 10% ethanol 20 0.816 95% ethanol 40 59.90 20 2.66 50% ethanol 40 8HA 95% ethanol 40 0.36 10% ethanol 40 0.19 [260] BHT 95% ethanol 40 0.27 [260] Propyl gallate 95% ethanol 20 0.27 [260] Propyl gallate 95% ethanol 20 0.27 [260] 95% ethanol 20 30.90 [260] 20 30.90 Propyl gallate 95% ethanol 20 30.90 [260] 1.02 95% ethanol 20 1.50 1.50 1.50 1.50		93 % ethanol	20	0.16	[300]
100 methanol 20 0.10 40 39.00 20 0.612 20 0.612 20 0.0756 20 0.0756 20 0.0756 20 0.816 20 0.816 20 0.816 20 2.66 50% ethanol 40 20 2.66 50% ethanol 40 20 0.00297 8HA 95% ethanol 40 0.27 20 0.00297 20 0.27 20% ethanol 0.27 20 0.27 20 0.27 20 0.27 20 0.27 20 30.90 20 30.90 20 30.90 20 30.90 20 30.90 20 30.90 20 1.50		50% othered	40	0.584	
Propyl gallate 95% ethanol 40 39.00 Propyl gallate 50% ethanol 20 0.612 50% ethanol 20 0.0756 20 0.0756 10% ethanol 20 0.816 10% ethanol 20 0.816 BHA 95% ethanol 20 2.66 50% ethanol 40 0.19 BHA 95% ethanol 40 0.19 BHT 95% ethanol 40 0.27 BHT 95% ethanol 20 0.266 10% ethanol 40 0.19 [260] BHT 95% ethanol 20 0.00297 50% ethanol 20 0.27 [260] $Propyl gallate$ 95% ethanol 20 30.90 $Propyl gallate$ 50% ethanol 20 30.90 20% 1.50 1.50 1.50		50% 601800	20	0.10	
Propyl gallate 20 0.612 40 1.28 20 0.0756 10% ethanol 40 2.78 10% ethanol 20 0.816 10% ethanol 20 0.816 BHA 95% ethanol 40 59.90 BHA 95% ethanol 40 0.36 50% ethanol 40 0.36 10% ethanol 40 0.19 BHA 95% ethanol 40 0.27 BHT 95% ethanol 20 0.27 60% ethanol 0.27 [260] Propyl gallate 95% ethanol 20 0.27 20 30.90 1.02 1.02 20% ethanol 20 30.90 1.50		95% ethanol	40	39.00	
Propyl gallate 30% ethanol 40 1.28 10% ethanol 20 0.0756 10% ethanol 20 0.816 BHA 95% ethanol 40 59.90 BHA 95% ethanol 40 59.90 BHA 60% ethanol 40 0.36 BHA 95% ethanol 40 0.36 BHA 95% ethanol 40 0.19 BHT 95% ethanol 40 0.00297 BHT 95% ethanol 20 0.27 $Propyl gallate$ 95% ethanol 20 0.27 $Propyl gallate$ 95% ethanol 20 30.90 Propyl gallate 95% ethanol 20 30.90 $Propyl gallate$ 50% ethanol 1.02 1.50		93 % ethanol	20	0.612	
Propyrgaliate 30% ethanol 20 0.0756 10% ethanol 40 2.78 20 0.816 BHA 95% ethanol 20 2.66 50% ethanol 40 0.36 10% ethanol 40 0.19 BHA 95% ethanol 40 24.10 95% ethanol 40 0.27 [260] BHT 95% ethanol 20 0.27 95% ethanol 20 0.27 [260] $Propyl gallate$ 95% ethanol 20 30.90 Propyl gallate 50% ethanol 40 1.02 $Propyl gallate$ 10% ethanol 20 30.90	Propul gallato	50% otherol	40	1.28	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	F TOPyr gallate	50 % ethanol	20	0.0756	
10% ethanol 20 0.816 20 59.90 20 2.66 50% ethanol 40 0.36 10% ethanol 40 0.19 20 0.00297 20 BHT 95% ethanol 40 0.27 20 0.27 [260] 20 0.27 [260] 20 0.27 [260] 20 0.27 [260] 20 0.27 [260] 20 30.90		10% othered	40	2.78	
BHA 40 59.90 BHA 20 2.66 $50%$ ethanol 40 0.36 $10%$ ethanol 40 0.19 BHT $95%$ ethanol 40 24.10 BHT $95%$ ethanol 20 0.00297 BHT $50%$ ethanol 20 0.27 $95%$ ethanol 20 0.27 [260] $Propyl gallate$ $95%$ ethanol 20 30.90 $Propyl gallate$ $50%$ ethanol 20 30.90 $Propyl gallate$ $50%$ ethanol 20 1.50			20	0.816	
BHA 20 2.66 50% ethanol 40 0.36 10% ethanol 40 0.19 95% ethanol 40 24.10 20 0.00297 20 BHT 95% ethanol 40 0.27 50% ethanol 20 0.27 [260] Propyl gallate 95% ethanol 20 30.90 Propyl gallate 50% ethanol 40 1.02 20 30.90 1.50 1.50		95% otherol	40	59.90	
BHA 50% ethanol 40 0.36 10% ethanol 40 0.19 40 24.10 95% ethanol 20 0.00297 20 0.27 [260] 50% ethanol 20 0.27 95% ethanol 20 0.27 95% ethanol 20 30.90 Propyl gallate 50% ethanol 40 1.02 95% ethanol 20 30.90 Propyl gallate 50% ethanol 40 1.02 10% ethanol 10 1.50	ВПУ	93 % ethanol	20	2.66	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	DIA	50% ethanol	40	0.36	
BHT 40 24.10 BHT 20 0.00297 50% ethanol 40 0.27 20 0.27 20 0.27 95% ethanol 40 176.00 20 30.90 95% ethanol 20 30.90 20 1.02 20 1.50		10% ethanol	40	0.19	
BHT 20 0.00297 50% ethanol 40 0.27 [260] 20 0.27 20 0.27 95% ethanol 40 176.00 100 Propyl gallate 95% ethanol 20 30.90 1000 ethanol 20 1.02 20		95% otherol	40	24.10	
M 40 0.27 [260] 20 0.27 [260] 95% ethanol 40 176.00 20 30.90 [20] Propyl gallate 50% ethanol 40 1.02 20 1.50	внт	93 % ethanol	20	0.00297	
20 0.27 95% ethanol 40 176.00 20 30.90 Propyl gallate 50% ethanol 40 1.02 20 1.50 1.50	ЫП	50% otherol	40	0.27	[260]
$\begin{array}{c c} 40 & 176.00 \\ \hline 20 & 30.90 \\ \hline 50\% \text{ ethanol} & 40 & 1.02 \\ \hline 20 & 1.50 \end{array}$		50 % ethanol	20	0.27	
Propyl gallate $\begin{array}{c} 20 & 30.90 \\ \hline 40 & 1.02 \\ \hline 20 & 1.50 \end{array}$		95% ethanol	40	176.00	
Propyl gallate 40 1.02 50% ethanol 20 1.50		93 % ethanol	20	30.90	
20 1.50	Propyl gallate	50% ethanol	40	1.02	
			20	1.50	
10% ethanol 40 0.79		10% ethanol	40	0.79	

Table 2-11 *D* coefficients reported of chemical compounds in different media and temperatures.

Compound	Media	T, °C	<i>Dx</i> 10 ⁻¹⁴ , m ² .s ⁻¹	Reference
1 nitrognicolo	phoophoto huffor	27	0.000052	[207]
4-1111021115018	priospirate buller	57	0.000048	[307]
Lidocaine	phosphate buffer	37	0.00008	[317]
Nifedipine	phosphate buffer	37	0.005640	[314]
Lidocaine	phosphate buffer	37	0.000004	[318]
Progesterone	water	37	0.051	[319]
	95% ethanol		0.000450	
Silver	10% ethanol	20	0.0023	[220]
Silver	water	20	0.045	[320]
	3% acetic acid		16.00	
Thyme oil	water bath	room	0.139	[321]
		20	0.049	
	OF% othered	30	1.31	
Catechin	95% ethanoi	40	4.79	
		50	3.15	
	50% ethanol	40	1.12	
		20	0.088	[308]
		30	1.37	[000]
	95% ethanol	40	5.12	
Epicatechin		50	3.49	
		10	0.044	
	50% ethanol	40	0.941	
Pinobanksin	water	25	8.90	
Pinobanksin-5-methyl-				
ether	water	25	10.30	[309]
<i>p</i> -coumaric acid	water	25	7.40	
Chrysin	water	25	7.55	
Pinobanksin	ethanol	25	14200.00	
		23	0.316	
α-tocopherol	ethanol	33	0.529	[310]
		43	3.80	

Compound	Media	T, °C	<i>Dx</i> 10 ⁻¹⁴ , m ² .s ⁻¹	Reference	
Resveratrol 1%	ethanol	9	0.00347	[312]	
		23	0.23		
		33	2.26		
		43	8.51		
Resveratrol 3%	ethanol	9	0.00349		
		23	0.306		
		33	4.17		
		43	8.26		
ВНТ	95% ethanol	23	0.295	[195]	
		31	0.895		
		43	19.00		
Astaxanthin	95% ethanol	30	1.27	[313]	
		40	2.28		
Epigallocatechin gallate	water	37	10.10	[311]	
Thymol	95% ethanol	30	29.00	[294]	
		40	60.00		
		50	163.00		
		60	57.50		
	15% ethanol	30	17.00		
		40	24.00		
		50	66.00		
		60	262.00		
Silver	10% ethanol	40	1.12	[252]	
Oligonucleotides	Phosphate buffer	37	0.00132		
				[315]	
	foetal calf serum	37	0.00137		
Hydrocortisone 4.8%			0.0417		
Hydrocortisone 12.1%	phosphate buffer	37	2.45	[323]	
Hydrocortisone 15.3%			11.40		
Hydrocortisone 25.8%			0.000547		
Compound	Media	T, °C	<i>Dx</i> 10 ⁻¹⁴ , m ² .s ⁻¹	Reference	
----------	-------------	-------	---	--	--
Thymol	10% ethanol		17.00		
			11.00 8.00		
			23.00		
		40	15.00	15.00 13.00 2700.00 2800.00 2600.00 3500.00 5500.00 7000.00	
			13.00		
	95% ethanol		2700.00		
			2800.00		
			2600.00		
			3500.00		
			5500.00		
			7000.00		

Table 2-11 (cont'd)

Diffusion of migrants in PLA is governed by the polymer FV and the size of migrant molecules [17,235,236]. On the other hand, the polarity and the affinity between the migrant compounds and PLA are important in the case of solubility [326]. Moreover, plasticization effects of migrant can also affect the migration by inducing changes in T_g or T_m of the polymer. A detailed discussion of these factors is out of scope for this review. Additional information can be found elsewhere [306,327,328].

It has been reported that the high polarity of 10% ethanol acted as a barrier preventing the release of α-tocopherol, butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT) and *tert*-butylhydroquinone (TBHQ) at 20 °C; however, this barrier was overcome at a higher temperature (40 °C) for BHA and TBHQ due to increases in their molecular mobility [306]. Certain organic solvents cause swelling of the PLA matrix, which creates void spaces in the polymer structure resulting in the promotion of the diffusion of chemical compounds. This is the case of PLA in contact

with ethanol, methanol, propanol, and butanol. For example, as ethanol acts as a plasticizer, the diffusion of α -tocopherol, BHA, BHT, propyl gallate, catechin, epicatechin and thymol increased [260,294,306,308]. Figure 2-33 shows migration of various compounds in ethanol (95% volume by volume) as a function of the compounds' M_w . The straight lines shown in the plot are linear least squares regression lines at each temperature. The current data did not show any trends in *D* as a function of M_w or temperature (data not shown).



Figure 2-33 Migration of organic compounds in ethanol (95% volume by volume). The straight lines shown in the plot are linear least squares regression lines at each temperature. References: thymol [316], butylated hydroxyanisole (BHA) [260], butylated hydroxytoluene (BHT) [195,260], propyl gallate [260], catechin [308], α-tocopherol [306], astaxanthin [313].

Polarity and solubility influence release rate of chemical compounds, due to the interactions of polymer, chemical compounds and simulants. For instance, faster release was observed for propyl gallate than for BHT into 95% ethanol at 40 °C, showing the effect of the molecular volume and polarity of the antioxidants. Also, faster release of BHA into 95% ethanol than 50% ethanol at 20 °C shows the influence of simulant polarity and antioxidant solubility [260,306]. No release of flavonoids was observed from PLA films to oil because of the limited solubility of the antioxidants in the medium, leaving the molecules trapped in the polymer matrix [308]. However, release of α -tocopherol from PLA to oil was observed due to the solubility of this antioxidant in fatty media, which promoted the interaction [310].

Regular solution theory (RST) was applied to predict the polymer-compoundsimulant interactions considering the absolute distances between the solubility parameters as dispersion (δ_D), polar (δ_P), and hydrogen (δ_H) bonding [195,297]; The greater the distance between the chemical compound, media and polymer matrix, the lower the affinity. Ortiz-Vazquez et al. [195] calculated the relative distance ($\Delta\delta$) of 2.37 MPa^{1/2} between PLA and BHT, 20.5 MPa^{1/2} between PLA and ethanol, 6.7 MPa^{1/2} between PLA and oil, and 26.1 MPa^{1/2} between PLA and water, indicating a higher affinity between PLA-BHT than PLA-solvents. The results were in accordance with nondetected release of BHT in water at 13, 23 and 43 °C.

2.11 Final remarks

Until now, more than 2,600 unique experimental mass transfer measurements have been recorded for PLA, providing a unique assessment of PLA barrier. Lacking

systematic review of the mass transfer of other polymers makes extensive comparison not possible. The only other polymer with so much reported mass transfer properties is PET, albeit without a systematic review of its mass transfer properties. Although a large number of barrier properties have been reported for PLA, most of these values were not reported with regard to the three-phase structure of semicrystalline PLA (i.e., CF, MAF and RAF). This is a large shortcoming of the reported barrier property values of PLA. However, it was not until the last decade that we started recognizing the three phases of most glassy polymers including common polymers such as PET. So, it is not the researchers' lack of understanding, but the general mass transfer field of glassy polymers that is being challenged with this new finding.

It has been established that the *P* values of gases in PLA follow this general order; $P_{CO_2}>P_{He}>P_{O_2}>P_{H_2}>P_{N_2}>P_{CH_4}$. For oxygen, P_{O_2} follows this order; LDPE>PS>PP>HDPE>PLA>PET>Nylon 6. For water vapor, P_{H_2O} follows this order; PLA>PS>PET>LDPE>PP>HDPE. Regarding organic vapors, limited values have been reported and additional research is needed. PLA with nanocomposites mostly shows some improvements in barrier properties, but PLA with additives and other treatments such as composites tend to worsen barrier properties, while results from blends vary.

Finally, there is a crucial need to consider the three-phase model when reporting the mass transfer properties of PLA. Characterization and determination of the free volume will be a strong addition when reporting mass transfer properties of PLA as well as other polymers. In summary, this comprehensive, critical and systematic review provides a unique mass transfer assessment of PLA to advance the commercialization and research of this distinctive bio-based and biodegradable polymer.

2.12 Acknowledgments

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CHAPTER 3

IN-SITU CHANGES OF THE THERMO-MECHANICAL PROPERTIES OF POLY(LACTIC ACID) FILM IMMERSED IN ALCOHOL SOLUTIONS

3.1. Abstract

Poly(lactic acid) (PLA) has properties suitable for several packaging, medical and agricultural applications. However, PLA's properties are affected by environmental conditions. In this study, the glass-rubber transition temperatures (T_g) of PLA films were measured during immersion (i.e., in-situ) in alcohols and alcohol aqueous solutions using a dynamic mechanical analysis technique. The T_g of PLA decreased when immersed in alcohols. For aliphatic alcohols, the T_g reduction became smaller as the number of carbons (C1–C10) in the alcohol main chains increased. The Fox equation and the Flory-Huggins (FH) model based on the Hansen solubility parameters (HSP) were used to explain the T_g reduction of PLA. The relationship explained the interactions between PLA and alcohols with small molecules (C1–C8), but bigger alcohols (C9–C10) did not fit the prediction. The chemical isomerism in propanol (i.e., 1and 2-propanol) did not affect the T_g reduction. The T_g reduction in 2-propanol aqueous solutions was concentration dependent although the partition coefficients based on the HSP and the FH interaction parameters did not fit this relationship. The *in-situ* immersion of PLA in alcohol solutions could be used to evaluate the change in T_g from the T_g of dry PLA, but more work is needed to correlate the T_g reduction with known parameters such as solubility parameters to predict PLA's T_g in other solvents.

3.2. Introduction

Poly(lactic acid) (PLA) – a biodegradable, compostable, and renewable polymer – is the most researched commercial bio-based polymer with properties that can be tailored by controlling its chiral structure composition [1,2]. Although PLA has been produced on a large scale since early 2005 [3] and it has been used in the medical, textile, agricultural, and packaging fields [1,4–6], it is a relatively new polymer and its properties are not yet fully comprehended. One concern for PLA is that its properties can be affected by the service and storage environments such as temperature, humidity, and contacted substances.

Changes in properties of PLA have been observed when PLA is in contact with solvents and solutions [7,8]. Effects of water vapor and liquid water on PLA have been extensively evaluated due to the inherent hydrolytic behavior of the PLA chemical structure [8–14]. PLA may also be exposed to organic solvents and aqueous solutions, resulting in swelling as well as changes in its morphological structure, and therefore, thermal and mechanical properties [7,8,15–19]. Evidence of solvent-induced crystallization in PLA, where permeation of selected solvents into the amorphous phase of PLA swells the polymer matrix and promotes crystallization, has also been shown [8,16,20,21].

Despite extensive studies on the effects of organic solvents and aqueous solutions on PLA morphologies, only a limited number of studies addressed the changes happening *in-situ*, that is when PLA is immersed in solvents. As the glass-rubber transition (T_g) measurement is one of the experimental methods used to determine plasticization effects of solvents on polymeric materials [22], some initial

information about *in-situ* changes of PLA's T_g in selected alcohols and aqueous solutions have been reported by Iñiguez-Franco et al. [8]. Using dynamic mechanical analysis (DMA) immersion equipment, they reported that the measured T_g of PLA dropped during immersion in ethanol and ethanol aqueous solutions and demonstrated that T_g decreased when the concentration of ethanol in aqueous solutions increased. In contrast, T_g of PLA measured after immersion in methanol and ethanol using a differential scanning calorimetry (DSC) technique [7,23] did not show significant reductions. These findings suggest that PLA undergoes a glass-rubber transition during immersion that is not observed after immersion.

A typical commercial grade PLA has a T_g around 58±2 °C [24], which is not much higher than room temperature in some regions of the world during summer months. Therefore, it is likely that PLA will be used at a temperature near its T_g , which may cause adverse effects on PLA properties. Additionally, it is possible that the solvents or solutions that PLA is in contact with will affect its T_g . To design suitable applications for PLA, it is necessary to understand and evaluate its useful temperature range, exposure to vapors and solvents, and the actual T_g during working conditions (i.e., *in-situ*). Alcohols are well-known food simulants, commonly present in medicines and alcoholic beverages, and likely to be in contact with PLA. Thus, alcohols were chosen as the solvents for this study.

The aim of this study was to determine the *in-situ* changes in PLA's thermomechanical properties when immersed in alcoholic solutions, including selected aliphatic alcohols with the number of carbons in the main chain from C1 to C10 (i.e.,

methanol to decanol), alcohols with different isomers (i.e., 1- and 2-propanol), and aqueous solutions of 2-propanol at different concentrations.

3.3. Experimental

3.3.1. Film production

PLA cast film made from PLA IngeoTM 2003D resin (NatureWorks, LLC, Minnetonka, MN, USA) was produced in a Randcastle Microtruder (Randcastle Extrusion Systems, Inc., Cedar Grove, NJ, USA) with a 1.5875 cm diameter screw, 34 cc volume and 24/1 L/D ratio at 193–215 °C and 49 rpm. PLA pellets were dried at 60 °C for 24 h prior to film processing. Thickness of the produced amorphous neat PLA film was 20±5 μ m. To minimize physical aging, the film was stored in a freezer (-20 °C) and preconditioned at 23 °C and 50% RH for 24 h immediately before use. The number average molecular weight (*M_n*), the weight average molecular weight (*M_m*), and the polydispersity index (PDI) of the film measured by size-exclusion chromatography (Waters 1515 Isocratic HPLC pump, Waters 717plus autosampler, and Waters 2414 refractive index detector, Waters Corporation, Milford, MA, USA) using tetrahydrofuran (Sigma-Aldrich, St. Louis, MO, USA) as a solvent were 95 kg/mol, 171 kg/mol, and 1.8, respectively.

3.3.2. Solvents

The solvents used for immersion tests were a series of selected aliphatic (straightchain) alcohols with the number of carbon atoms C1–C10 (i.e., methanol, ethanol, 1propanol, 1-butanol, 1-hexanol, 1-octanol, 1-nonanol, and 1-decanol), a branched chain
alcohol C3 (2-propanol), and water. A mixture of 50% (v/v) 2-propanol in water was used as an alcoholic aqueous solution. Except for 1-octanol and 1-decanol, which were purchased from EMD-Millipore (Burlington, MA, USA), solvents were purchased from Sigma-Aldrich (St. Louis, MO, USA). All solvents were used as received. Table 3-1 shows the properties of the solvents.

Solvent	#C	Melting point ^a , K (°C)	Boiling point ^a , K (°C)	Molar mass ^a , g	Molar volume ^b , mL/mol	Purity ^a
water	-	273 (0)	373 (100)	18.0	18.0	≥99.9%
methanol	1	175 (-98)	338 (65)	32.0	40.6	≥99.9%
ethanol	2	156 (-117)	351 (79)	46.1	58.6	≥99.9%
1-propanol	3	146 (-127)	370 (97)	60.1	75.1	≥99.5%
2-propanol	3	184 (-89)	355 (82)	60.1	76.9	≥99.5%
1-butanol	4	183 (-90)	391 (118)	74.1	92.0	≥99.4%
1-hexanol	6	221 (-52)	430 (157)	102.2	125.2	≥98.0%
1-octanol	8	257 (−16) °	368 (195) ^c	130.2	158.2	≥99.0%
1-nonanol	9	265 (-8)	488 (213)	144.3	174.9	≥98.0%
1-decanol	10	279 (6) ^c	505 (232) ^c	158.3	191.8	≥99.0%

Table 3-1 Solvents used for immersion tests and their properties.

^a From manufacturers' data sheets, unless noted otherwise. ^b From HSPiP software [25]. ^c From CRC Handbook of Chemistry and Physics [26]. #C = number of carbon atoms in alcohol main chains.

3.3.3. Thermal and thermo-mechanical property measurements

Differential scanning calorimetry (DSC): A differential scanning calorimeter DSC Q100 (TA Instruments, New Castle, DE, USA) calibrated with indium standards was used to measure the thermal properties of PLA films before immersion. Film samples of 5–10 mg were weighed and sealed in a TA Instruments hermetic aluminum pan and the thermal analysis was performed under nitrogen atmosphere with a flow rate of 70 mL/min. In the first heating cycle, the sample in a sealed pan was equilibrated at 20 °C, cooled to –50 °C, heated from –50 to 200 °C, and remained isothermal for 1 min. Then, the system continued to the second heating cycle where the sample was cooled to –50 °C and finally heated to 200 °C. The temperature ramp rate for all the cycles was 10 °C/min. The samples were tested at least in triplicate. The results were analyzed with the TA Instruments Universal Analysis 2000 software version 4.5A and the T_g values were determined from the inflection point at the step change in the DSC thermogram.

Dynamic mechanical analysis (DMA): An RSA-G2 Solids Analyzer (TA Instruments, New Castle, DE, USA) DMA unit was used to measure the thermo-mechanical properties of PLA films before and during (*in-situ*) immersions. The RSA-G2 settings were as follows: loading gap 15 mm, max gap changes up 5–10 mm, max gap changes down 1 mm, preload force 100 g, strain 0.2%, frequency 1 Hz, and temperature ramp rate 5 °C/min. For each DMA experiment, a 10 mm x 50 mm film sample was mounted to the tension clamps. The DMA temperature ramp started at 25 °C for dry film and for the *in-situ* water and aqueous solution immersions, and –5 to 10 °C for the *in-situ* pure

alcohol immersions. Liquid nitrogen and air, connected to the RSA-G2's forced convection oven, were used for cooling and heating. The temperature ramp ended at approximately 20 °C above the temperature at peak tan(delta). For the *in-situ* immersion experiments, the RSA-G2 immersion cell was installed. The solvent was precooled to the desired starting temperature and poured into the immersion cell that contained a mounted sample. Once the required starting temperature was reached, the temperature ramp started. The samples were tested at least in triplicate. The storage modulus, loss modulus, and tan(delta) data were obtained and the results were analyzed with TRIOS software version 4.5.0 (TA Instruments, New Castle, DE, USA). The peak tan(delta) value was recorded as the film's T_g .

3.3.4. Statistical analysis

Statistical significance was determined by analysis of variance (ANOVA) and the mean comparisons were determined by Tukey's HSD (honestly significant difference) tests using SAS analytics software University Edition (SAS Institute Inc., Cary, NC) at a significance level of 0.05.

3.4. Results and discussion

3.4.1. Pre-immersion properties

Figure 3-1a shows a typical DMA result for a dry PLA sample (pre-immersion) including the storage modulus, loss modulus, and tan(delta) (i.e., the ratio of the loss modulus to the storage modulus). The T_g for pre-immersion PLA samples measured from peak tan(delta) was 62.9±1.0 °C. Figure 3-1b shows a typical second heating scan of a pre-

immersion PLA sample from the DSC. As determined from the DSC, the T_g , the cold crystallization temperature (T_c), and the melting temperature (T_m) were 60.6±0.1 °C, 126.1±0.5 °C, and 150.9±0.3 °C, respectively. The crystalline fraction (X_c), the mobile amorphous fraction (X_{MAF}), and the rigid amorphous fraction (X_{RAF}) determined from the DSC as described by Magoń and Pyda [27] were 0.5±0.2%, 78.8±5.1%, and 20.7±4.9%, respectively. The low X_c indicates that the film was practically amorphous and that the X_{RAF} should not affect the evolution of T_g [28,29]. The T_g values of dry PLA film measured from DMA and DSC are statistically different at a significance level of 0.05. Since the measured T_g can depend on the instrument settings such as the heating rates and test frequencies [30], a slight difference is expected.



Figure 3-1 Typical pre-immersion (dry sample) test results of PLA from a) dynamic mechanical analysis (DMA) and b) differential scanning calorimetry (DSC). T_g , T_c , and T_m are glass-rubber transition, cold crystallization, and melting temperatures, respectively.

3.4.2. Effects of solvent sizes

Figure 3-2 shows the *in-situ* immersion test results of PLA in a series of aliphatic alcohols where the tan(delta) is plotted against the temperature. Comparing the peak tan(delta) values, the T_g of PLA is lower when immersed in alcohol with lower number of carbon atoms in the main chain, implying that smaller straight-chain alcoholic molecules can diffuse faster through the free volume region of PLA. This agrees with a general observation that an increase in the size of the compound in a homologous series (i.e., straight-chain alcohols with increasing number of carbons) results in a decrease in the diffusion coefficient through a polymer matrix [31]. Interactions of the alcohol molecules with PLA cause swelling and plasticization of the PLA matrix, leading to an increase in mobility of the PLA chain and thus a decrease in the T_g .

Trailing peaks are observed at around 64 °C from tan(delta) of alcohols C8–C10. While these peaks may be attributed to partially plasticized PLA films showing another T_g value close to the T_g of the dry film, they could be due to the sample and instrument limitations. At the temperature range where these peaks appeared, the film was softened and the elongation of the film was beyond the maximum allowed gap between the tension clamps, which was limited by the enclosed oven. Using thicker film samples might help to reduce the film elongation to within the restricted gap, but thick films could result in a nonuniform distribution of the solvent molecules within the PLA matrix. Additional tests are needed to validate these peaks and to determine a practical film thickness that best compromises between the film elongation and the solvent distribution issues. Furthermore, the high temperature tests were not conducted in alcohols C1–C6 since most of the solvents would be evaporated.



Figure 3-2 Tan(delta) of PLA films in different aliphatic alcohols as a function of temperature.

The drop in the T_g from the T_g of dry PLA is plotted in Figure 3-3 to show the trend as the number of carbon atoms and molecular volumes of the solvents changed. More discussion on the changes in the T_g is provided in Section 3.4.4.



Figure 3-3 Changes in the T_g values of the *in-situ* immersed PLA films in aliphatic alcohols (circle markers, showing average values and standard deviation bars with $3 \le n \le 6$) from the T_g of dry PLA (horizontal dash line) as a function of number of carbons and molecular volumes of the solvents. Values shown below the circle markers are percent T_g reduction in Celsius from the T_g of dry PLA.

The T_g of PLA immersed in 1-decanol is statistically higher than the T_g of dry PLA. This could be due to the high viscosity of 1-decanol as well as different thermal conductivity of the liquid from that of the air, i.e., the conditions when the film was heated in liquid were different from when the dry film was directly exposed to the heated air. Since alcohols larger than 1-decanol are solid at room temperature, they were not tested. However, if the instrument setup for heating solid alcohols is possible, testing PLA in alcohols with larger molecules is recommended to verify the increase in T_g .

Additional experiments were conducted to compare the T_g of PLA after immersion and detailed discussion is provided in Appendix A. The results show varying values of post-immersion T_g (i.e., the film samples were immersed in solvents, wiped dry, and measured for T_g). These findings emphasize that the post-immersion T_g measurements may not capture the actual T_g during the time PLA is exposed to the solvents.

3.4.3. Effects of branching and concentration

Some preliminary tests were performed to evaluate the factors affecting the T_g reduction of PLA when immersed in branched-chain alcohols and alcohol aqueous solutions. The findings from these selected alcohols may not be extrapolated to other alcohols, but this section should provide some initial understanding of PLA properties in these alcohols as well as the factors affecting PLA's T_g .

Effects of branching of propanol: To compare the effects of the solvent chemical structures on T_g , 1-propanol (a straight-chain alcohol) and 2-propanol (a branched-chain alcohol) were selected as solvents. These two alcohols are structural isomers with 3 carbon atoms and the same chemical formula. For typical alcohols with small number of carbons, a linear alcohol is more tightly packed than its branched isomer(s) [32], e.g., the molecular volumes of 1- and 2-propanol are 75.1 and 76.9 mL/mol, respectively. However, Figure 3-4 shows that the T_g values of PLA when immersed in 1-propanol and 2-propanol were not different. The result suggests that the branched and shorter chain in 2-propanol does not affect the solvation of PLA and the reduction of T_g . Also, the difference in molecular volumes of 1- and 2- propanol may not be large enough to result in different T_g values.



Figure 3-4 Tan(delta) of PLA film in 1-propanol and 2-propanol as a function of temperature. Numbers #1 and #2 show replicates of each experiment.

Effects of solvent concentrations: The results for PLA *in-situ* immersion in water, 2propanol, and 50% (*v/v*) 2-propanol aqueous solution are shown in Figure 3-5. Compared to the T_g of PLA film before immersion, the reduction in T_g is largest in pure (100%) 2-propanol and the T_g reduction becomes smaller as the concentration of 2propanol in water decreases. This finding may imply concentration dependency of the mass transfer of 2-propanol in PLA. These T_g reduction trends are in good agreement with the results previously reported by Iñiguez-Franco et al. [8] that T_g of PLA dropped from 60 °C before immersion to 36 °C when immersed in 50% ethanol and that T_g decreased when the concentration of ethanol in aqueous solutions increased. However, a linear relationship was not prominent as can be seen from the inset in Figure 3-5. Further testing is needed to identify the difference in behaviors of PLA film in different alcohol and water solutions.



Figure 3-5 Tan(delta) of PLA film in water, 2-propanol and 50% (v/v) 2-propanol aqueous solution as a function of temperature. The inset shows T_g as a function of 2-propanol fraction with a linear trendline.

3.4.4. Modelling relationship between the solvent molecules and the

changes in the T_g of PLA

The T_g values measured by DMA pre-immersion and *in-situ* immersion in alcohols, alcohol solutions, and water are summarized in Table 3-2. Statistical comparisons of the T_g values in straight-chain alcohols, marked with lowercase letters, show that T_g values are different in different alcohols. The T_g values in 1- and 2-propanol are not statistically different, as marked by the same uppercase letter. Finally, comparisons of the T_g values at dry conditions and in 50% 2-propanol, 100% 2-propanol, and water, marked with Greek letters, show that all T_g values were statistically different.

Solvent	<i>T_g</i> , °C	T_g reduction, %
none (no immersion)	62.9±1.0 ^{a, α}	-
methanol	14.3±0.9 ^b	77
ethanol	25.3±0.6 °	60
1-propanol	29.6±0.8 ^{d, A}	53
2-propanol	$30.0\pm1.5^{A, \beta}$	52
50% (<i>v/v</i>) 2-propanol	33.6±0.3 ^v	47
1-butanol	34.3±0.4 ^e	45
1-hexanol	41.0±0.1 ^f	35
1-octanol	45.7±1.9 ^g	27
1-nonanol	49.8±1.1 ^h	21
1-decanol	64.0±0.5 ⁱ	-2
water	$53.3\pm0.5^{\delta}$	15

Table 3-2 A summary of T_g of PLA film sample immersed in different solvents.

Note: Uppercase, lowercase, and Greek letters indicate different comparisons based on Tukey's HSD tests at a significance level of 0.05. Values with the same letter(s) are not different.

A relationship between the T_g of a polymer and the plasticization effect of a low molecular weight compound is usually estimated based on the additivity of basic thermo-physical properties such as the Fox, Gordon-Taylor, or Kelley-Bueche equation. The prediction of the T_g of PLA in different solvents by the Fox equation [33] is illustrated in Figure 3-6. Detailed calculations are shown in Appendix B. Comparing the experimental and the predicted T_g values, only a small fraction of the solvent was absorbed into PLA. The Fox equation prediction shows that none of the weight fractions of solvents in PLA exceed 0.1, with methanol having the highest weight fraction in PLA (0.08) and water having the lowest value (0.02). Other alcohols C2–C6 have weight fractions in PLA in the range of 0.05–0.06. The T_g values of alcohols with C>6 are not available; therefore, the estimations for these alcohols were not included.



Figure 3-6 Glass transition temperatures (T_g) prediction of PLA in alcohols. The lines show predicted T_g of PLA being plasticized by different alcohols based on the Fox equation [33], compared with the corresponding experimental T_g values shown by markers in the same colors as the lines. The numbers C1–C6 indicate the number of carbon atoms in the alcohol main chains and C3b denotes 2-propanol.

The reduction in the T_g of PLA when immersed in alcohols may be explained by the interactions of alcohols with PLA where the small molecular weight alcohols plasticize the PLA matrix resulting in PLA segmental chain movements, and thus a lower value of the measured T_g . Lindvig et al. [34] proposed a Flory-Huggins (FH) model based on the Hansen solubility parameters (HSP) to assess the FH interaction parameters, χ_{12} , of a solvent (denoted by subscript 1) and a polymer (denoted by subscript 2). The model can be expressed as shown in equation (1) where α^* is an empirical factor that needs to be estimated from experimental data, V_1 is the molar volume of the solvent, *R* is the gas constant, *T* is the temperature in Kelvin, δ_d , δ_p , and δ_h are the HSP based on the contributions from the dispersion, polar, and hydrogen bonding, respectively. The HSP values for PLA and the solvents used for the immersion tests are listed in Appendix B.2. The values used for our calculations were adjusted to the measured *in-situ* T_g values. An arbitrary α^* value of 0.6 was chosen for the current prediction as previously demonstrated as a good estimation [34].

$$\chi_{12} = \alpha^* \frac{V_1}{RT} \Big((\delta_{d1} - \delta_{d2})^2 + 0.25 \big(\delta_{p1} - \delta_{p2} \big)^2 + 0.25 \big(\delta_{h1} - \delta_{h2} \big)^2 \Big)$$
(1)

The predicted interaction parameters between PLA and different solvents were plotted against the experimental T_g from the *in-situ* immersions as shown in Figure 3-7. The χ_{12} values are higher for smaller alcohols and lower for bigger alcohols (i.e., longer chain, higher number of carbons). However, for alcohols larger than C8, the χ_{12} values do not decrease as the *in-situ* T_g values increase. The trend corresponds well with the prediction from the Fox equation shown in Figure 3-6. However, the parameters used for the calculation were obtained from different sources based on different experimental setups, so they may not directly be correlated to the established trend. Further investigations should be focused on validating the empirical values used for the prediction and confirm whether the prediction is reliable. Additional tests with 1-pentanol and 1-heptanol to confirm this trend will be useful.



Figure 3-7 The glass transition temperature (T_g) of PLA immersed in aliphatic alcohols as a function of the predicted interaction parameters (χ_{12}) at T_g . The numbers C1–C10 indicate the number of carbon atoms in the aliphatic alcohol main chains, W denotes water, and C3b denotes 2-propanol. The fitted exponential decay is shown as a dash line.

Similar calculations based on the Fox equation for water and 2-propanol in PLA

(Figure 3-8) show that water and 2-propanol reach their corresponding experimental T_g

values at the solvent weight fractions of 0.02 and 0.06, respectively.



Figure 3-8 Glass transition temperatures (T_g) prediction of PLA in 2-propanol and water. The lines show predicted T_g of PLA being plasticized by water and 2-propanol based on the Fox equation [33], compared with the corresponding experimental T_g shown by markers.

The partition coefficients K of solute (denoted by subscript *i*) in liquid (denoted L) and PLA (denoted P) can be estimated from the interaction parameters (Equation 1), as shown in Equation 2

$$\ln K_{i,L/P} = r_L^{-1} + \chi_{i,P} - \chi_{i,L}$$
(2)

where r_L is the ratio of the liquid volume to the solute volume. *K* of 2-propanol between water and PLA is 88 at infinite dilution. The reciprocal of this value is K of 2-propanol in PLA which is 0.01, which is much lower than the predicted weight fraction (~0.06) from the Fox equation. More experiments at different 2-propanol concentrations as well as in different aqueous solutions are needed to elucidate the effect of solvent concentrations.

3.5. Conclusion

PLA's T_g decreased when immersed in alcohols and alcohol aqueous solutions. The number of carbon atoms and the concentrations of alcohols in aqueous solutions directly affected the T_g reduction (i.e., a larger alcohol induces a smaller T_g reduction). However, the chemical structure of alcohol did not affect the reduction in T_g for different isomers of propanol. The trend in T_g reduction of PLA in alcohols and alcohol aqueous solutions correspond well with the calculations based on the known values of HSP for low molecular weight alcohols C≤8, but this relationship does not apply to higher molecular weight alcohols (C>8). Further experiments are required to establish the underlying phenomena for the *in-situ* PLA immersion in alcohol solutions as well as to predict PLA's T_g when immersed in other solutions.

APPENDICES

Appendix A: Post-immersion properties

The post-immersion experiments at different temperatures and immersion durations were performed to investigate the influence of solvents on the thermal and thermomechanical properties of PLA films using dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC).

A.1 Sample preparations

For post-immersion at 23 °C, the film samples were cut to a required size of 10 mm x 50 mm for the DMA or a required weight of 5–10 mg for the DSC and immersed in 50 mL glass vials. Each vial contained a solvent with a film sample being held in place by a stainless-steel wire and glass beads to ensure contacts with the solvent on both sides of the film [35]. The vial was then closed with a plastic cap and stored at room temperature (23±1 °C) for different durations (e.g., 20 min, 3 d, 6 d, 12 d). For post-immersion at elevated temperatures, the film samples were immersed in the RSA-G2 immersion cell and the temperature was controlled within ±1 °C by an attached force convection oven for 20 min. The 20 min post-immersion tests were performed to simulate the duration of the *in-situ* immersion tests while the immersion temperatures were selected based on the expected T_g of PLA from the *in-situ* immersion. For each post-immersion sample, once the required immersion duration was reached, the film was removed from the solvent and wiped dry with soft, low-lint tissues before testing. To preserve the state of the film after contact with the solvent, the film was tested without further drying or conditioning. The DMA and DSC measurements of post-immersion samples then

followed the pre-immersion sample (i.e., dry film) test procedures as described in Section 3.3.3.

A.2 Post-immersion results from DMA

Figure A-1 shows the T_g values of the pre-immersion (dry, control film) and the postimmersion (wiped-dry film) from the DMA in the y-axes and the number of carbon atoms in alcohol main chains and their molecular volume in the x-axes. The T_g for postimmersion in methanol (C1), ethanol (C2), butanol (C4), and 1-nonanol (C9) at 23 °C for 20 min did not change from the dry T_g . For post-immersions in 1-butanol (C4), T_g reductions were observed after 6 d and 12 d. For 1-nonanol, the size of the solvent might impede the sorption of the solvent into PLA matrix at 23 °C, as can be seen from no change in T_g from the dry PLA's T_g regardless of the immersion duration. Immersion experiments at elevated temperatures resulted in crumpled samples which were difficult to wipe dry without damaging the samples, and thus were not tested in the DMA.



Figure A-1 T_g of PLA from the DMA's peak tan(delta) post-immersion (wiped-dry) in different alcohols as a function of number of carbon atoms and molecular volume. The immersion temperature and duration were listed in the plot legend, with C representing number of carbon atoms.

A.3 Post-immersion results from DSC

Post-immersion samples were also tested in the DSC and the T_g values determined from the first heating cycle are summarized in Figure A-2. The results showed scattered data and unexpected high T_g values (i.e., higher than T_g of dry PLA) of PLA postimmersion in methanol (C1). While anti-plasticization effects have been cited as the cause of unexpected changes in polymer properties including increases in T_g of polymers in contact with low molecular weight species [36], this is unlikely the case for PLA in methanol in this immersion study. The results also show T_g reductions of PLA when immersed in alcohols at elevated temperatures, implying that both temperature and duration affected the drops in T_g after immersion. However, the results from postimmersion are not consistent. The DSC thermograms in Figure A-3 show a widened transition range for PLA post-immersion in methanol and the evaluated T_g values could be due to the unsteady state of the mass transfer period. Scattered results could be attributed to sample handling after immersion. The different amounts of solvent remaining in the film and on the film surface could affect the measured T_g . The T_g values from the second heating cycle after immersion shown in Figure A-4, however, did not vary by the type of solvent. Research by Sato et. al [7] showed a small variation of T_g of post-immersion PLA films in alcohols at 35 °C and 24 h measured by DSC when they dried the film under a vacuum for 48 h at 70 °C prior to the DSC characterizations. They found the post-immersion T_g values were not much different from the T_g of dry PLA, but solvent-induced crystallization occurred after immersion.



Figure A-2 T_g of PLA from DSC post-immersion (wiped-dry) in different alcohols as a function of number of carbon atoms and molecular volume; a) C1, C2, C4, and C9 at various temperatures and 20 min, b) C4 and C9 at 23 °C and various durations. The immersion temperature and duration were listed in the plot legend, with C representing number of carbon atoms.



Figure A-3 Thermograms of the first heating cycle of dry (control) PLA film and PLA films after immersions in different alcohols at 23 °C for 20 min. C represents number of carbon atoms.



Figure A-4 Thermograms of the second heating cycle of dry (control) PLA film and PLA films after immersions in different alcohols at 23 °C for 20 min. C represents number of carbon atoms.

Appendix B: Detailed calculations

B.1 Fox equation

The Fox equation (Equation B-1) was used for prediction of T_g reduction when PLA film is exposed to different solvents.

$$\frac{1}{T_g^*} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$
(B-1)

where T_g^* is the T_g of the mixture, w₁ and w₂ are weight fractions of component 1 and 2, respectively. T_{g1} and T_{g2} are T_g of component 1 and 2, respectively. The T_g values of alcohols used for the calculations are listed in Table B-1.

Solvent	#C	<i>T_g</i> , K (°C)
water ^a	-	136 (-137)
methanol b	1	102.6 (-170.4)
ethanol ^b	2	96.9 (-176.1)
1-propanol ^b	3	99.7 (-173.3)
2-propanol c	3	115 (-158)
1-butanol ^b	4	111.5 (-161.5)
1-hexanol ^b	6	129.7 (-143.3)
1-octanol	8	n/a
1-nonanol	9	n/a
1-decanol	10	n/a

Table B-1 The glass transition temperature (T_g) values of alcohols used for the Fox equation calculations.

^a From [37], ^b from [38], ^c from [39], n/a = not available.

#C = number of carbon atoms in alcohol main chains.

B.2 Hansen solubility parameters

The values of δ_d , δ_p , and δ_h of the solvents used in this study are listed in Table B-2. These values were recalculated to account for the temperature where the *in-situ* immersion T_g of PLA was observed based on equations B-2–B-4 using the HSPiP software [25] and the adjusted values are shown in Table B-3, where α is the thermal expansion coefficient. The HSP for PLA were based on the values reported by Elangovan et al. [40]. The HSP values of water used for the calculation are from water 1% soluble (i.e., small amount of water) instead of the values for bulk water (with δ_d , δ_p , and δ_h values 15.5, 16.0, and 42.3, respectively) since the very high δ_h of bulk water resulted in a high interaction parameter, which was difficult to use to correlate the experimental results with other solvents.

$$\frac{d\delta_d}{dT} = -1.25\alpha\delta_d \tag{B-2}$$

$$\frac{d\delta_p}{dT} = \alpha \frac{\delta_p}{2} \tag{B-3}$$

$$\frac{d\delta_h}{dT} = -(1.22 \times 10^{-3} + \frac{\alpha}{2})\delta_h \tag{B-4}$$

Solvent	#C	δ_{d} , MPa ^{1/2}	δ_p , MPa ^{1/2}	δ_h , MPa ^{1/2}	χ_{12} at 25 °C
PLA	-	17.6	5.9	6.5	-
water	-	15.1	20.4	16.5	0.37
methanol	1	14.7	12.3	22.3	0.80
ethanol	2	15.8	8.8	19.4	0.68
1-propanol	3	16.0	6.8	17.4	0.55
2-propanol	3	15.8	6.1	16.4	0.53
1-butanol	4	16.0	5.7	15.8	0.55
1-hexanol	6	15.9	5.8	12.5	0.37
1-octanol	8	16.0	5.0	11.0	0.33
1-nonanol	9	16.0	4.8	11.0	0.35
1-decanol	10	16.0	4.7	10.5	0.33

Table B-2 The Hansen solubility parameters (HSP) for PLA [40] and solvents used for immersion [25] and the calculated Flory-Huggins interaction parameters (χ_{12}).

#C = number of carbon atoms in alcohol main chains.

Table B-3 The adjusted Hansen solubility parameters (HSP) for PLA and solvents used
for immersion, the thermal expansion coefficients of liquid (α), and the calculated Flory
Huggins interaction parameters (χ_{12}) at the measured PLA <i>in-situ</i> immersion glass
transition temperature (T_g).

Solvent	#C	α, 1/°C	δ_d^* ,	δ_p^* ,	δ_h^* ,	r_{co} at T_{c}
			MPa ^{1/2}	MPa ^{1/2}	MPa ^{1/2}	λ12 α 19
PLA	-	0.00007 ^a	17.5	5.9	6.2	-
water	-	0.0009 ^b	14.6	20.1	15.7	0.32
methanol	1	0.0012 ^b	14.7	12.3	22.3	0.85
ethanol	2	0.0012 ^b	15.8	8.8	19.4	0.68
1-propanol	3	0.0011 ^b	16.0	6.8	17.4	0.58
2-propanol	3	0.0011 °	15.8	6.1	16.4	0.53
1-butanol	4	0.0010 ^b	16.0	5.7	15.8	0.56
1-hexanol	6	0.0009 ^d	15.9	5.8	12.5	0.37
1-octanol	8	0.0008 ^d	16.0	5.0	11.0	0.32
1-nonanol	9	0.0008 ^d	16.0	4.8	11.0	0.33
1-decanol	10	0.0008 ^d	16.0	4.7	10.5	0.34

^a From reference [2], ^b From reference [41], ^c from reference [39], ^d from reference [42], * values adjusted to the PLA *in-situ* T_{g} . #C = number of carbon atoms in alcohol main chains.

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CHAPTER 4

OVERALL CONCLUSION AND RECOMMENDATIONS FOR FUTURE WORK

4.1. Overall conclusion

The amount of research on poly(lactic acid) (PLA) regarding its properties has been increasing in the past decades; however, research focusing on its mass transfer properties is scarce. Many of the reported mass transfer properties of PLA in literature were parts of PLA characterizations, and thus lack systematic evaluation of the barrier properties.

Chapter 2 of this dissertation provides a comprehensive, systematic, and critical review of the experimental data of mass transfer properties of PLA to gases, vapors, and organic compounds. A recent finding of the three-phase structure in semicrystalline polymers, which consists of the crystalline, mobile amorphous, and restricted (or rigid) amorphous fractions contradicts a traditional and simple two-phase structure (i.e., crystalline and amorphous fractions). This three-phase model helps to explain unexpected barrier properties such as an increase in gas permeability in PLA when the degree of crystallinity increases [1], which is counterintuitive since crystalline regions are impermeable to gases and vapors. The de-densification of the restricted amorphous fraction in PLA [2] explains this behavior well. Lack of systematic experiments for PLA barrier properties assessment, especially for organic compounds and vapors, was also addressed in Chapter 2. This finding led us to propose a study for the interaction of PLA with organic solvents in the next chapter.

In Chapter 3, the *in-situ* immersion experiments of PLA in various alcohol solutions were conducted and reported. The glass transition temperature (T_g) of PLA decreased from the T_g of dry PLA when PLA was immersed in alcohol and alcohol aqueous solutions. The highest T_g reduction was in methanol, which is the smallest, lowest molecular weight aliphatic alcohol. The changes in T_g became smaller for the bigger, higher molecular weight aliphatic alcohols. The Hansen solubility parameters (HSP) and the Flory-Huggins (FH) interaction parameters [3,4] were then used for the prediction of T_g reduction and were found to be useful for alcohols with the number of carbon atoms in the main chain up to C8. The T_g reduction in bigger alcohols did not follow the prediction well. Isomers of propanol with straight and branched chains did not show any difference in T_g reduction, but without further experiments this finding alone may not imply that the location of hydroxyl group in alcohols or the packing of alcohol chains does not affect the interaction between PLA and alcohols. The concentration of 2-propanol in water affected the T_g reduction of PLA; the higher the 2-propanol concentration, the larger the T_g reduction. However, while previous work [5] showed a linear trend for concentration dependency of PLA in ethanol aqueous solutions, results for PLA in 2-propanol solutions from this study deviated from linearity. The use of the partition coefficient based on the HSP and FH parameters did not explain the behavior of PLA in aqueous solution either. More work is needed to determine the underlying phenomena when PLA is immersed in a binary mixture. The measurements of T_g postimmersion, where the films were wiped dry before the tests, showed that the PLA sample's conditions during in-situ immersion and post-immersion could be different and could result in much different T_g values. Thus, the *in-situ* immersion test is

recommended for the evaluation of the actual T_g of PLA when it is in contact with solvents.

4.2. Recommendations for future work

Based on the comprehensive literature review in Chapter 2, extensive research is essential to fill data gaps in the mass transfer properties of PLA. Overall, except for oxygen and moisture barriers, mass transfer of other gases and vapors in PLA have not yet been much investigated. Even for oxygen and moisture that were commonly assessed for their barrier properties, not to mention other less researched gases and vapors, systematic studies on factors affecting their mass transfer in PLA are lacking. Extrinsic factors such as temperature and relative humidity and intrinsic factors such as PLA crystallinity and L- and D-lactide contents, as well as other factors such as modifications of PLA by incorporation of additives, nanoparticles, or blends of PLA with other polymers, must be evaluated in the aspect of how they affect PLA barrier properties to different gases and vapors. Attention should be paid to the three-phase structure of PLA, whether the PLA sample under investigation is affected by the threephase structure behaviors (e.g., de-densification of the restricted amorphous fraction) and whether the barrier properties should be explained based on the three-phase structure.

To avoid the complications from the three-phase structure, amorphous PLA samples were used for the *in-situ* immersion of PLA in alcohol solutions experiments (Chapter 3). Further investigations using semicrystalline PLA samples are recommended to evaluate whether the solvents and PLA interact differently in the
presence of crystallinity in PLA. Furthermore, because the *in-situ* immersion experiments were conducted in selected solvents with different melting and boiling points, the starting and ending points for the temperature ramp varied for different solvents. Even though this variation was assumed to have no effects on the test results, more investigation may be needed to validate the assumption. Additionally, effects on the viscosity of the solvents as well as whether the temperature in the immersion cell is uniform (i.e., whether the temperature read by the thermocouple and the temperature of the film in the solvent are the same) should be investigated. Our *in-situ* immersion results from 1-decanol (C10) imply no further T_g reduction in larger aliphatic alcohols. Nevertheless, due to the instrument limitations, conducting experiments with alcohols that are solid at room temperature such as 1-dodecanol (C12) was not feasible. If instrumental setup allows for larger alcohols to be tested, it is recommended. Further investigations on the isomerism effects should be conducted, for example, on 1- and 2butanol and isobutanol. Additional concentrations of 2-propanol in water are required to fully understand the effect of the solvent concentrations to T_g reduction. Aqueous solutions of other alcohols should also be investigated.

The *in-situ* immersion experiments on other families of solvents such as ketones, esters, ethers, aldehydes, aromatic and non-aromatic hydrocarbons should be conducted and compared to the results from the alcohol family. In addition to gaining more understanding of PLA behaviors when immersed in these solvents, correlating the changes in properties of PLA to known properties of solvents such as the molecular volume or the solubility parameters may help to confirm whether our prediction is useful. However, parameters used for the prediction should be evaluated carefully since values

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from different sources or different testing methods can be significantly different and will affect the prediction results.

Overall, there are many areas in mass transfer properties of PLA to be explored. Even for a specific scope such as the *in-situ* immersion of PLA in alcohol solutions, there are still many questions that have not been answered. With the advance in technology and the knowledge sharing in the polymer science community, hopefully more accurate predictions of PLA properties based on known parameters could be done to help extend PLA usage to different applications without the need for extensive experiments. REFERENCES

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