

**RELEASE KINETICS OF α -TOCOPHEROL AND RESVERATROL FROM
POLY(LACTIC ACID) AND POLY(LACTIC ACID)/STARCH BLENDS**

By

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ABSTRACT

RELEASE KINETICS OF α -TOCOPHEROL AND RESVERATROL FROM POLY(LACTIC ACID) AND POLY(LACTIC ACID)/STARCH BLENDS

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The aim of this study was to investigate the use of poly(L-lactic acid) (PLLA) as active functional membranes for application in food and pharmaceutical packaging system.

PLLA films containing various concentrations of α -tocopherol (α -TOC) and resveratrol were fabricated, and the influence of the antioxidants on the optical, thermal, mechanical, rheological, and physical properties of PLLA films were assessed. PLLA films with added α -TOC and resveratrol showed a yellowish brown color and the light transmission properties were influenced by the presence of the antioxidants. The glass transition (T_g) and melting (T_m) temperatures were significantly reduced with the addition of antioxidants while thermal stability was enhanced. The concentrations of the two antioxidants played a critical role in the mechanical and thermo-mechanical properties of PLLA films. The melt viscosity of the PLLA films with added antioxidants was substantially higher than that of neat PLLA films. Second, maleic anhydride (MAH) was grafted onto PLLA resin in the presence of dicumyl peroxide (DCP) as a radical initiator. The effect of the MAH and DCP concentrations on the grafting and the physical and mechanical properties of PLLA films were investigated. Introduction of MAH reduced the gel content and increased grafting yield. The T_g and crystallinity (X_c) significantly decreased on addition of MAH. The thermal decomposition of the PLLA films was decreased with addition of MAH while the mechanical properties were almost unchanged. Third, PLLA/starch blends were

prepared by a one step reactive compatibilization process. The effect of the grafting reaction on the physical, mechanical, and morphological properties of PLLA/starch blend was assessed. Little effect of the maleation reaction on the thermal stability of the PLLA/starch blends was observed. PLLA/starch blends with grafted MAH showed significant decrease of T_g due to the plasticizing effect of MAH. Reactive compatibilization resulted in increase of storage modulus, E' of PLLA/starch blends indicating that compatibility between two phases increased by reactive compatibilizer. Good interfacial adhesion between PLLA and starch was found in the blends. Fourth, PLLA/starch blends with various concentrations of α -TOC and resveratrol were fabricated, and the effects of two antioxidants on the optical (color), thermal and mechanical properties of PLLA/starch blends were assessed. PLLA/starch blend films with α -TOC and resveratrol showed a yellowish color influenced by the combined effect of the white starch and brown antioxidants. The T_g and T_m were significantly reduced with the addition of antioxidants while enhanced thermal stability was observed. The release of resveratrol from PLLA and PLLA/starch blend films into ethanol followed Fickian behavior with D values between $0.073 \sim 0.54 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$, $0.90 \sim 3.44 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$, and $24.8 \sim 74.3 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA films; and $1.42 \sim 6.93 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$, $4.16 \sim 22.3 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$, and $40.1 \sim 309.0 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA/starch films, respectively at 13, 23, 43 °C. D values of α -TOC were $0.47 \sim 4.0 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$, $5.67 \sim 13 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$, and $89.0 \sim 118.0 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA films; $0.70 \sim 6.83 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$, $4.10 \sim 24.2 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$, and $123.0 \sim 282.0 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA/starch films, respectively at 13, 23, 43 °C.

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This dissertation is dedicated to my dearest family, Jeong Yeon Lee and Ji Woo Hwang

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KEY TO SYMBOLS OR ABBREVIATIONS

<i>Symbols</i>	<i>Key</i>
E_a	Activation energy
α -TOC	Alpha tocopherol
AFM	Atomic Force Microscopy
BP	benzoyl peroxide
BHT	Butylated hydroxytoluene
CO ₂	Carbon dioxide
cm	Centimeter
C	Concentration
°C	Degree Celsius
DCP	Dicumyl peroxide
DSC	Differential Scanning Calorimeter
D	Diffusion coefficient
DMA	Dynamic Mechanical Analyzer
A_G	Elasticity Coefficient
EVOH	Ethylene vinyl alcohol copolymer
FCS	Food Contact Substance
FTIR	Fourier Transform Infrared Spectroscopy
ω	Frequency
GPC	Gel Permeation Chromatography
GPa	Gigapascal
T_g	Glass transition temperature
g	Gram
Hz	Hertz

HDPE	High density poly(ethylene)
HSD	Honesty Significant Difference
<i>J</i>	Joules
LLDPE	Linear low density poly(ethylene)
<i>G''</i>	Loss modulus
LDPE	Low density poly(ethylene)
MAH	Maleic anhydride
MPa	Megapascal
<i>T_m</i>	Melting temperature
m	Meter
μg	Microgram
μm	Micrometer
mg	Milligram
mm	Millimeter
nm	Nanometer
<i>M_n</i>	Number average molecular weight
O ₂	Oxygen
<i>K_{p,s}</i>	Partition coefficient
Pa	Pascal
PHA	Poly(3-hydroxyalkanoate)
PHBV	Poly(3-hydroxybutyrate)-co-(3-hydroxyvalerate)
PBAT	Poly(butylene adipate-co-terephthalate)
PCL	Poly(ε-caprolactone)
PET	Poly(ethylene terephthalate)
PLA	Poly(lactic acid) or Poly(lactide)
PLLA	Poly(L-lactic acid) or Poly(L-lactide)

PMMA	Poly(methyl methacrylate)
PP	Poly(propylene)
PDXL	Polydioxolane
PEG	Polyethylene glycol
PS	Polystyrene
PVOH	polyvinyl alcohol
RH	Relative humidity
SEM	Scanning Electron Microscopy
s	Second
±	Standard deviation
G'	Storage modulus
TS	Tapioca Starch
TGA	Thermo Gravimetric Analyzer
TPS	Thermoplastic Starch
UPLC	Ultra Performance Liquid Chromatography
USFDA	United States Food and Drug Administration
H ₂ O	Water
M_w	Weight average molecular weight
η_o	Zero shear viscosity

CHAPTER I

CHAPTER I

Introduction

For the most part, plastics have replaced traditional materials used in packaging applications because of their physical properties such as tensile strength, toughness, lightness, and barrier properties which could meet specific packaging requirements[1]. The current global consumption of plastics is more than 250 million tons with a 5% annual growth rate[2].

However, the increasing plastic consumption has increased plastic waste, and increased environmental concerns due to their long-lasting presence in the environment. Additionally, the incineration of plastic waste produces a large amount of carbon dioxide or toxic gases, which have been known to cause pollution. The extent of petroleum resources are also becoming limited[3]. Therefore, great attention has been given to develop renewable source-based biodegradable plastic materials to replace petroleum based plastics, especially for short-term packaging, pharmaceutical, and disposable applications. The market share of global bioplastics is currently under one percent, and is growing in many different fields such as packaging and agricultural films[2]. Figure 1.1 shows a sketch of the life cycle of bioplastics[2].

Poly(lactic acid) (PLA) is one of the most promising biobased polymers because it can be made from agricultural products and is readily biodegradable[4]. PLA is already commercialized and has good mechanical properties, thermal plasticity, and biocompatibility, so it has been used in medical implants, sutures, drug-delivery systems, as well as being commercially available for single-use disposal items[4-6]. PLA has been approved as polymer for use in food-contact articles[7]. Currently, additional research is being conducted to provide active packaging properties to PLA membranes[8].

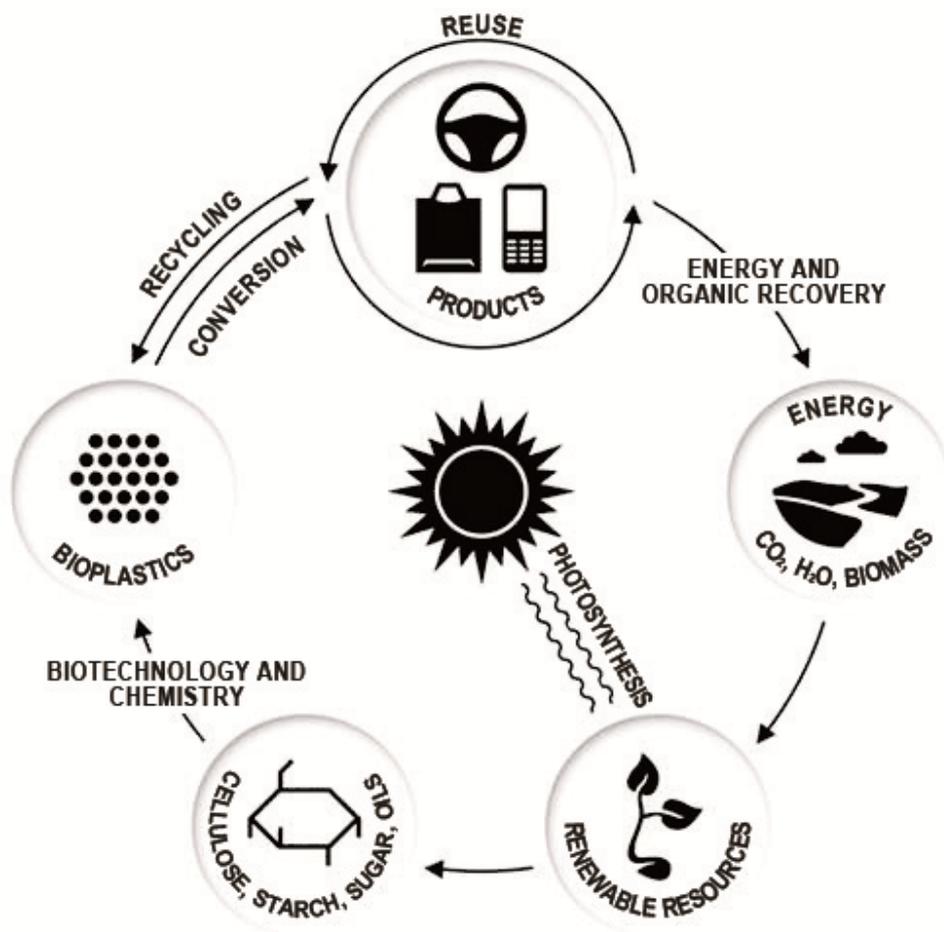


Figure 1.1 Life cycle of bioplastics, Adapted from www.european-bioplastics.org [2]

Although PLA is an eco-friendly attractive material for the packaging applications, there are limitations for the use of specific applications. Some of the PLA limitations for packaging applications are its brittle nature with less than 10 % elongation at break[9, 10], and its processing instability. Furthermore, PLA undergoes degradation due to hydrolysis at elevated temperatures, and it also has low melt viscosity, which may limit its blow molding or foaming processability. Therefore, PLA bulk or surface modification or blends with other polymers are mainly considered the way to improve toughness and other properties such as degradation rate, roughness, and hydrophilicity[11]. Branching or crosslinking of PLA during melt processing

with modifiers are representative modification techniques. This could improve processability for blow molding or foaming by increasing the molecular weight and melt viscosity of PLA. Several research groups have studied blends of PLA with poly(ϵ -caprolactone) (PCL)[10, 12]. PLA and PCL are known to be immiscible blends, but it was found that PCL domains could be well dispersed into the PLA matrix through efficient mixing procedures[12]. PLA nanocomposites were developed with organically modified layered silicate, and remarkably improves the mechanical and other properties compared to neat PLA[3]. Copolymerization of PLA with polyethylene oxide (PEO) resulted in increasing the flexibility of the PLA/PEO multiblock copolymer by using PLA-PEO-PLA block copolymer as a coupling agent[13]. Reactive compatibilization is another approach to improve compatibility of PLA with other polymers by chemical reaction of two polymers during their blending[14-16]. Many have reported that maleic anhydride (MAH) could be easily grafted into polyolefin in the presence of an initiator during melt processing[17-21]. Several researchers have also reported the use of MAH for grafting monomers or oligomers onto polyolefin molecule chains resulting in a bridge between MAH and the polymer chains to improve interfacial adhesion[17, 19, 20]. The improvement of toughness could play a key role in both food and pharmaceutical for successful packaging applications. Recent strategies for the enhancement of toughness will be covered in chapter II.

The addition of antioxidants into polymers has attracted many researchers as an alternative to direct mixing of antioxidants with food stuffs since increasing the levels of additives in the food formulation is restricted by FDA regulations. Furthermore, higher antioxidant concentrations could result in pro-oxidation reactions in lipids. An antioxidant packaging system is a system in which antioxidants are released at a controlled rate to retard lipid oxidation. This system has great potential to extend the shelf life of products by maintaining

a constant and effective concentration of the antioxidant inside of the package. Butylated hydroxytoluene (BHT), a synthetic antioxidant, has been often introduced in liners of cereal packages[22]. However, the current trend in use of antioxidants is to change to natural antioxidants which are considered safer for humans.

Diffusion and solubility of antioxidants are important factors in packaging systems, and the relationships among the release rate of the antioxidants, package, and food type are complex. Therefore, understanding the release kinetics of antioxidants from a variety of packaging materials is critical in order to develop packaging systems for specific food and/or pharmaceutical products under different environmental conditions.

1.1 Goal and Objectives

The goal of this dissertation is to develop PLLA and PLLA/starch blends containing two antioxidants, α -tocopherol (α -TOC) and resveratrol, in order to develop active functional membranes for food and pharmaceutical packaging systems.

The objectives of this study are:

1. To develop and produce PLLA films with added two natural antioxidants, α -TOC and resveratrol at different concentration levels
2. To determine the effect of the addition of these two natural antioxidants on the optical, physical, thermal, and mechanical properties of PLLA
3. To prepare PLLA-g-MAH and PLLA/starch blends by a reactive compatibilization technique
4. To assess the compatibility, physical and mechanical properties of PLLA-g-MAH and PLLA/starch blends

5. To determine the releasing kinetics of α -TOC and resveratrol from PLLA/antioxidant film and PLLA/starch/antioxidant blend film samples into a food stimulant, ethanol at three different temperatures

In order to accomplish the objectives mentioned above, the experimental work conducted in this PhD dissertation was divided into four phases.

Phase I: Preparation of PLA with added α -TOC and Resveratrol

PLLA films containing two natural antioxidants, α -TOC and resveratrol with various concentrations were fabricated by melt compounding and compression molding processes. The influence of the antioxidants on the optical, color and UV-VIS light transmission, and thermal properties was analyzed. The mechanical, thermo-mechanical and rheological properties of the films were also assessed.

Phase II: Preparation of PLA-g-MAH as a compatibilizer for PLA/starch blends

MAH was grafted onto PLLA, PLLA-g-MAH, in the presence of dicumyl peroxide (DCP) as an initiator, and the dependence of MAH grafting reaction onto PLA on the concentration of DCP and MAH was investigated. The thermal and mechanical properties were assessed to determine the optimized concentration of DCP and MAH as a potential compatibilizer for PLLA blends.

Phase III: Preparation of PLLA/starch blends by reactive compatibilization

PLLA/starch blends were prepared with different compositions by a reactive compatibilization technique with a fixed amount of MAH (2.0 phr) and DCP (0.1 phr). The PLLA/starch blend sample was cooled down to room temperature, and then compression molded to form a film. The thermal, mechanical, rheological, and morphological properties were evaluated to assess the compatibility of the PLLA/starch blends.

Phase IV: Preparation of PLLA/starch blends with added α -TOC and resveratrol and migration study of PLLA and PLLA/starch blend films

PLLA/starch blends with α -TOC and resveratrol were fabricated, and the effects of the two antioxidants on the optical, color, thermal, and thermo-mechanical properties were analyzed. In addition, migration of α -TOC and resveratrol from the PLLA and PLLA/starch blends film to a food simulant was assessed using migration cells filled with ethanol and stored at three different temperatures for a period of time enough to reach steady state of migration. Diffusion coefficients of antioxidants from the PLLA and PLLA/starch blend film samples to ethanol at three different temperatures were determined through non-linear regression modeling with MATLAB analysis.

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CHAPTER II

CHAPTER II

Literature review

2.1 Introduction

Today, the role of packaging is not only to extend the shelf life of the product but also to contribute to the safety and functionality of the food system. Among packaging materials, polymers especially have contributed significantly to the advancement of packaging technology. Understanding polymer structure and properties is important for tailoring polymers for specific packaging applications.

This chapter aims to provide a literature review of the basic theory and function of controlled release packaging, lipid oxidation, and antioxidants. It also covers the structures and properties of PLA and starch as base polymers for development of the controlled antioxidant release packaging system. Various recent approaches such as reactive modification and blends to enhance the flexibility and toughness of PLA are discussed.

2.2 Controlled release packaging systems

2.2.1 Active packaging

As consumer demands increased for safe and fresh products, new packaging systems have been developed to maintain the high quality of food products and extend shelf life. A packaging system provides functions such as containment, protection, convenience, and communication. Much interest has been given to enhance protection and convenience. One of the developed packaging technologies to enhance these functions of packaging is active packaging systems. The term "Active packaging" was first used by Labuza in 1987[1]. After that Hotchkiss, (1995) [2] defined active packaging as '*the packaging system providing some demanded functions in*

addition to barrier function to external environment. Robertson, (2005) [3] recently redefined active packaging as "the packaging in which subsidiary constituents have been deliberately included in either the packaging material or the package headspace to enhance the performance of the package system."

According to Ahvenainen, (2003) there are two main types of active packaging system technologies[4]. The first type is absorbing or scavenging systems and the other consists of releasing systems. Scavenging systems are designed to remove or to absorb undesired substances such as oxygen, carbon dioxide, ethylene, humidity or other compounds such as off-flavors, while the releasing systems are created to emit compounds such as antioxidants and antimicrobial agents into the headspace of the package for improving the quality and safety of products. Scavenger and releasing systems can be made of sachets, labels, or functional membranes. Sachets are normally placed inside of the package while labels can be adhered directly on the internal wall of the package. Furthermore absorbers or scavengers and releasers can be incorporated into the film so that they are released in the headspace or migrate into the package[5].

2.2.2 Controlled release packaging

Controlled release packaging systems have been developed and used extensively for pharmaceutical applications, specifically for drug delivery[6, 7]. In recent years, research on the application of controlled release systems in food packaging has increased since they enable controlled release of active compounds like antioxidants to be delivered at specific rates during storage, in order to maintain a specific concentration of the antioxidant that will assure the protection and extension of the shelf life of food products.

A simplified representation of a controlled release packaging system is illustrated in Figure 2.1. The active layer is the one containing the active compounds that will be released into the package (food and/or pharmaceutical products).

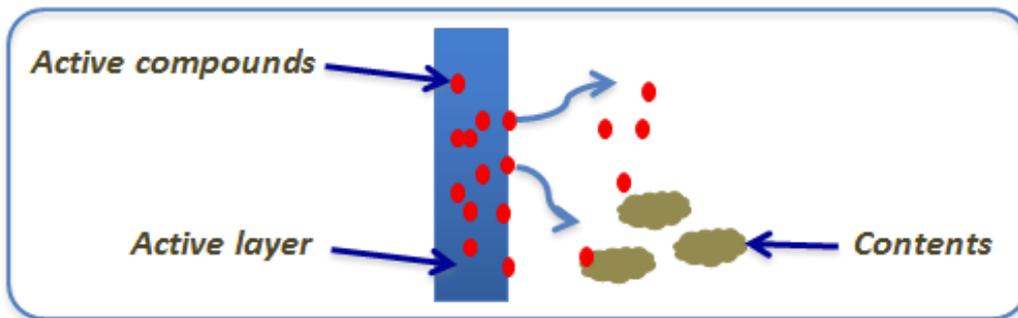


Figure 2.1 Controlled release package system. For interpretation of the references to color in this and all other figures, the reader is referred to the electronic version of this dissertation

The release profiles of controlled release packaging materials can be categorized into zero and first order release[8]. A zero-order release system is where the active compound is released at a constant rate independent of active ingredient concentration until the active ingredient is depleted. The release time is proportional to the amount of active compound contained in the package. In the first order release system, the active compound release rate depends on the active ingredient concentration, and declines exponentially as the active ingredient concentration approaches zero[8]. The equations for zero- and first-order release kinetics are presented in equations (1) and (2).

$$Q_t = Q_0 - k_0 t \quad (1)$$

$$\begin{aligned} \ln(Q_t) &= \ln(Q_0) - k t \\ \text{Log} Q_t &= \text{Log} Q_0 - k t / 2.303 \end{aligned} \quad (2)$$

where Q_0 = initial amount of antioxidant

Q_t = cumulative amount of antioxidant release at time t

k_0 = zero-order release constant

k = first-order release constant

t = time

In general the mechanism of antioxidant release involves three steps: 1) the antioxidant diffuses through the polymer bulk phase to the polymer surface; 2) the antioxidant volatilizes from the polymer surface to the package headspace or desorbs from the polymer surface; and 3) the antioxidant migrates or adsorbs onto the product's surface[9].

A variety of active ingredients such as antioxidants have been incorporated into various packaging materials to assess the potential controlled release action of polymer/antioxidant system since both packaging materials and the packaged product can be obtained benefits. In the packaging material the presence of antioxidant provides protection to the polymer during processing while once the active ingredient is within the package it will be released and inhibit the product's oxidation and/or degradation[10]. In addition, controlled antioxidant release packaging can maintain higher quality in foods and pharmaceuticals over longer periods of time. This is believed to be more efficient than direct addition of antioxidants into food during processing[11].

Han *et al.* (1998) investigated the controlled release kinetics of potassium sorbate by using various materials such as poly(ethylene) (PE), poly(propylene) (PP), and poly(ethylene terephthalate) (PET). The prediction and estimation of the releasing profile of the potassium

sorbate through plastic films were assessed mathematically[12]. It was found that LDPE had the highest diffusivity as compared to other films. Therefore in this specific case LDPE is a good material to be included in the control layer for the fast release of potassium sorbate while other films are good to be included in the control layer for a slow release.

Buonocore *et al.* (2005) developed a cross-linked polyvinyl alcohol (PVOH) single layer film and a multilayer film structure composed of cross-linked PVOH single layers, and investigated the release kinetics of lysozyme, an antimicrobial agent[13]. The multilayer films showed a slower release rate of lysozyme compared to the single layer film. The potential application of lysozyme in controlled release packaging to slow down the bacterial growth in food packaging was confirmed. Recently, Gemili *et al.* (2009) showed the suitability of using asymmetric cellulose acetate (CA) films for controlled release of lysozyme without compromising the mechanical properties[14].

Miltz *et al.* (1988) reported that HDPE film with a high concentration of butylated hydroxytoluene (BHT) added extended the shelf-life of oatmeal cereal packaged in HDPE bags as compared to cereal packaged in a film with a low concentration of BHT[15].

Wessling *et al.* (1998) studied the migration and sorption behavior of α -TOC and BHT in LDPE in contact with fatty food simulant. They found that the migration of α -TOC into the food simulants was slower than that of BHT due to the slower movement of α -TOC as compared to BHT. This suggested that α -TOC would be a suitable replacement for BHT as an antioxidant in polymers[16].

Byun *et al.* (2010) prepared PLA antioxidant film with α -TOC, BHT, and polyethylene glycol 400 (PEG 400) by a film casting technique. PLA film with BHT and PEG 400 (BP-PLA) had antioxidant activity due to the presence of BHT; however, it had less antioxidant activity

than PLA film with α -TOC, BHT and PEG 400 (ABP-PLA). The antioxidant activity of the ABP-PLA film was significantly increased by the addition of α -TOC into the BP-PLA film[17].

Soto-Cantú *et al.* (2008) investigated the release of BHT added LDPE film as a core layer in polyamide 6 (PA6) and 66 (PA66) multilayer film, and it was found that release of BHT from the film added with 8 mg.g^{-1} of the antioxidant added in the LDPE layer complied with the legal limit[18].

Granda-Restrepo *et al.* (2009) prepared multilayer films composed of high density polyethylene (HDPE), ethylene vinyl alcohol (EVOH), and LDPE containing butylated hydroxyanisole (BHA), BHT, and α -TOC. It was found that BHA and BHT migrated faster from the multilayer films to the milk powder while α -TOC showed slow migration. BHT has relatively higher mobility than α -TOC due to its small molecular size, therefore it has a tendency to migrate rapidly from packaging materials into foods[19].

Manzanarez-López *et al.* (2011) reported that the diffusion of α -TOC from PLA films to ethanol simulant follows Fickian behavior with diffusion coefficients (D) at levels between $3.16 \pm 0.19 \times 10^{-11}$ and $5.29 \pm 0.71 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ at 23 and 33 °C, respectively. They also suggested the potential production of PLA packaging with α -TOC for protection of oily foods[20].

2.3 Poly(lactic acid)

2.3.1 Synthesis and structure

Poly (lactic acid) (PLA) can be made from agricultural products, and it is biodegradable and compostable[21]. PLA is generally manufactured by ring-opening polymerization of lactide as monomer. Lactide is the cyclic dimer prepared by the controlled depolymerization of lactic acid,

which is obtained by the fermentation of dextrose obtained from corn, sugar cane, and sugar
beats[22, 23].

There are two approaches to produce PLA, condensation polymerization of lactic acid and ring opening polymerization of lactide. High molecular weight PLA is difficult to produce by the direct condensation polymerization of lactic acid since it is difficult to control the dehydrative equilibrium for the esterification or the formation of PLA having a high molecular weight[24]. Hartmann obtained high molecular weight PLA without the use of chain extenders or adjuvants by azeotropic dehydrative condensation of lactic acid[25]. The synthetic methods to obtain high molecular weight PLA are shown in Figure 2.2. Ajioka *et al.* (1998) also produced high molecular weight PLA with a direct solution condensation process in which lactic acid, catalysts, and organic solvent with a high boiling point were mixed and reacted for relatively long reaction times[26, 27]. Moon *et al.* (2000) investigated the effect of different types of catalysts on melt condensation polymerization, and it was reported that tin oxide and chloride could be effective in the production of high molecular weight PLA[28]. They also successfully produced high molecular weight PLLA with the melt/solid polycondensation of L-lactic acid catalyzed by both tin chloride dehydrate and p-toluenesulfonic acid[29].

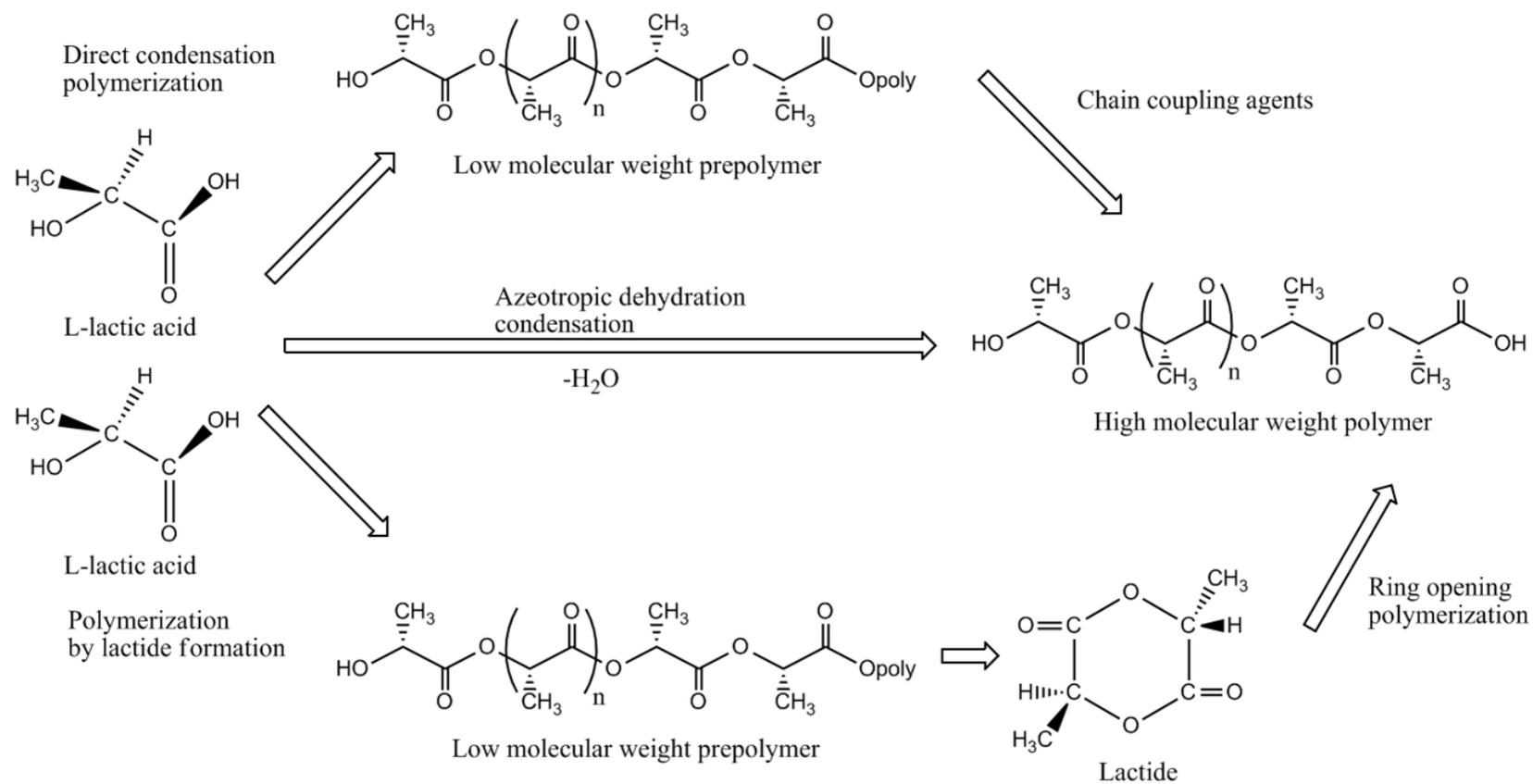


Figure 2.2 Synthesis methods for high molecular weight PLA, adapted from [25]

The ring opening polymerization through lactide formation is the current method used by NatureWorks LLC to produce high molecular weight PLA for commercial applications[30]. The ring-opening polymerization can be initiated by a methyl trifluoromethanesulfonic or trifluoromethanesulfonic acid (triflic acid)[31, 32], or initiated by the nucleophilic reaction of the anion with the carbonyl, with subsequent acyl-oxygen cleavage[31-33].

Commercial PLA is a copolymer of poly (L-lactic acid) (PLLA) and poly (D-lactic acid) (PDLA) or poly (D,L-lactic acid) (PDLLA) obtained from L-lactide, D-lactide, and *meso* or D,L-lactide, respectively, so a copolymer is produced from the polymerization of L-lactide and D,L-lactide[30]. The chemical structure of each lactide and PLA are presented in Figure 2.3 and 2.4. The ratio of D- to L- enantiomers and the arrangement of the monomer chains are mainly responsible for the physicochemical properties of PLA. PLA with higher optical purity (> 93% of L-lactic acid) tends to be semicrystalline while that with lower optical purity is amorphous.

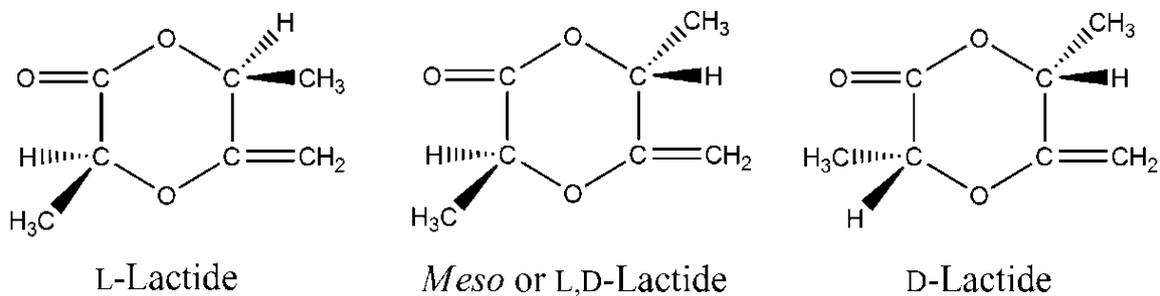


Figure 2.3 Chemical structure of L-, *meso*-, and D-lactides, adapted from [30]

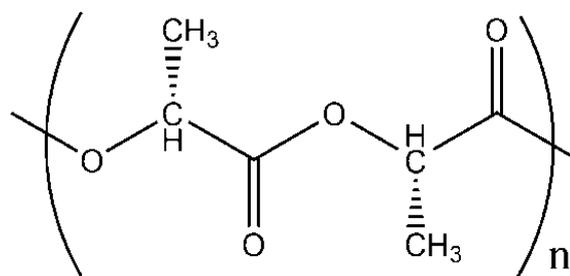


Figure 2.4 Chemical structure of PLLA

2.3.2 Thermal properties

The glass transition temperature (T_g), the melting temperature (T_m), and percent crystallinity of PLA decrease with decreasing amounts of PLLA[24, 34-36]. Auras *et al.* (2004) reported that PLA has T_g , and T_m ranging from 50 to 80°C and 130 to 180°C, respectively[30]. The T_g , and T_m values with other typical thermoplastic polymers are given in Figure 2.5.

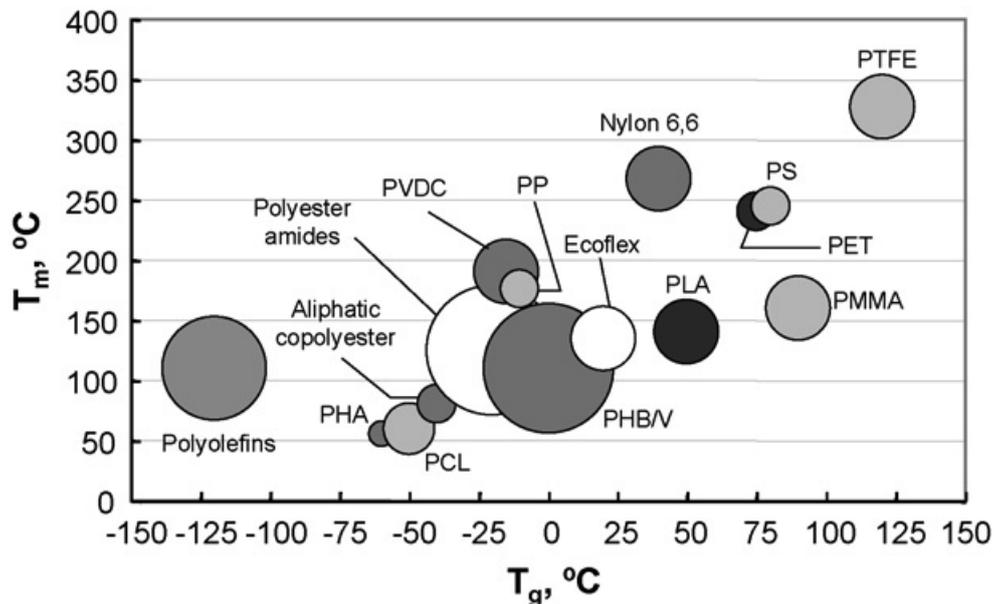


Figure 2.5 The T_g , and T_m of PLA and other polymers, adapted from Lim *et al.*[36]

It can be seen that PLA shows relatively higher T_g , and T_m as compared to other biodegradable polymers, but presents lower T_g , and T_m as compared to other petroleum based polymers except olefins[36]. PLA with higher content of L-lactide has higher T_g values than PLA with the same amount of D-lactide[37]. The T_g , and T_m of PLA obtained from different ratios of copolymer are shown in Table 2.1.

Table 2.1 Transition temperature of selected PLA copolymers, adapted from Bigg [38]

PLA copolymer ratio	Glass transition temperature(°C)	Melting temperature(°C)
100/0 (L/D,L)	63	178
95/5 (L/D,L)	59	164
90/10 (L/D,L)	56	150
85/15 (L/D,L)	56	140
80/20 (L/D,L)	56	125

The thermal history is one of the factors affecting T_g of PLA. Generally, PLA quenched from the melt state with a high cooling rate results in an amorphous polymer due to the limitation of crystal growth.

It was reported that the thermal history strongly affects the physical properties of PLLA, resulting in changes of crystalline: amorphous ratio, and PLLA with low crystallinity showed a rapid aging with time at ambient conditions[39]. Tsuji and Sawada reported that the physical aging of amorphous PLLA at low temperature (below T_g) increased the T_g and enthalpy at T_g , and physical aging at 50 °C caused accelerated crystallization of PLLA[40].

It was reported that the optical purity of PLA has great effect on the melting behavior of PLA. The stereo-chemically pure PLA shows the T_m of 180 °C with an enthalpy of 40 ~ 50 J·g⁻¹, and the presence of meso-lactide in PLA can decrease the T_m up to 50 °C depending on the content of D-lactide[36]. The relationship between T_m and meso-lactide content could be approximately calculated by the following equation (3) proposed by Witzke[41].

$$T_m (\text{°C}) \approx 175\text{°C} - 300 \cdot W_m \quad (3)$$

where W_m is the fraction of meso-lactide, and 175 °C is the T_m of PLA obtained from 100% L-lactide. Understanding the effect of meso-lactide content on the T_m of PLA is important not only to extend processing windows, but also to decrease thermal and hydrolytic degradation[36].

2.3.3 Optical properties

The ultraviolet- visible (UV-visible) light transmission properties of a packaging film is an important property that needs to be considered when designing packaging systems in order to protect the contents. For example, transmitted UV and visible light had great effect on changes the flavor and nutrition values of milk[42]. The wavelength ranges are normally between 200 and 2,200 nm; UV range of 100 ~ 400 nm, visible range of 400 ~ 700 nm, and near infrared region of 700 ~ 2,200 nm, respectively[30].

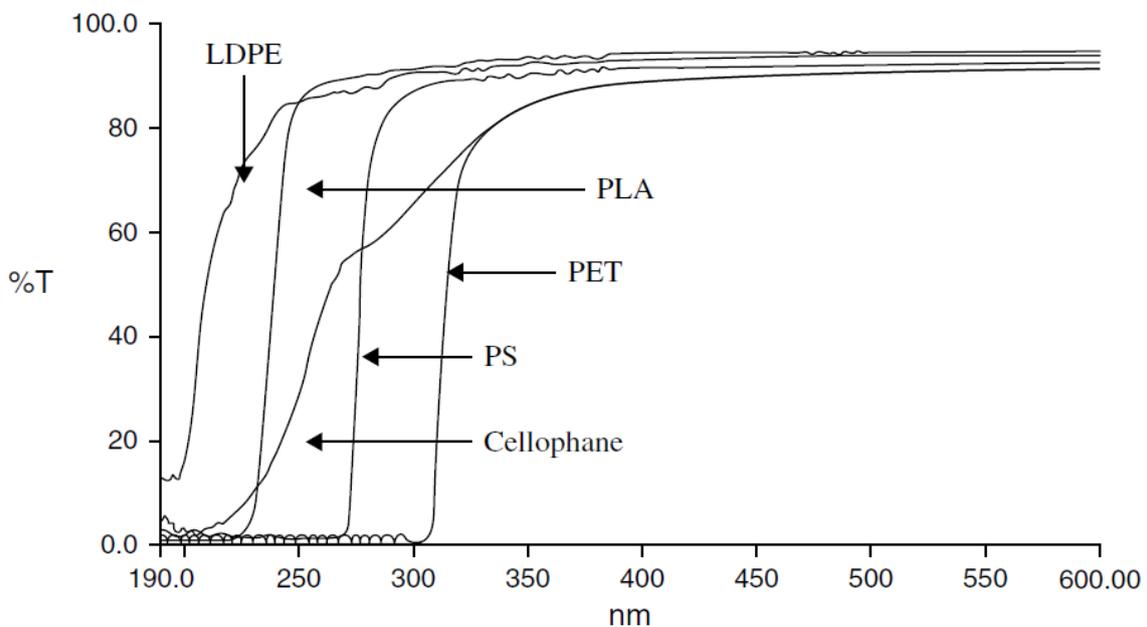


Figure 2.6 Percent transmission of PLA, PS, LDPE, PET and cellophane films, adapted from Auras, *et al.* [30]

PLA light transmission properties have been researched and compared with commercial polystyrene, poly(ethylene terephthalate), low density polyethylene, and cellophane films in the range 190 ~ 800 nm. As seen in Figure 2.6, no UV transmission was found in the UV range of 190 ~ 220 nm wavelength region. PLA starts to transmit UV light at 225 nm, and increases up to 85% at 250 nm. For complete block of UV, UV stabilizer would be required for dairy food products, especially for light sensitive food[30].

Fourier transform infrared spectroscopy (FT-IR) analysis could be used to provide a chemical profile of a polymer material; when an infrared beam is focused on a film sample; different amounts of light are absorbed at different wavelengths depending on the chemical composition of the sample. General peak assignments for PLA are presented in Table 2.2.

Table 2.2 General peak band assignments of PLA, adapted from [30, 33, 43].

Functional group	Vibrational mode	Wave number (cm ⁻¹)
CH ₃ , C-C	CH ₃ torsion, skeletal C-C torsion	300
-	amorphous and crystalline phase of PLA	871, 756
CH ₃	helical backbone vibrations with CH ₃ rocking	956, 921
C-O-C	C-O-C stretching	1090 (asym)
C-O	C-O stretching	1225
CH	C-H bending	1315, 1300
CH	C-H deformation	1382 (deform), 1365 (asym)
C=O	C=O stretching	1759
CH ₃ , CH	C-H stretching	2997 (asym), 2946 (sym), 2877

(sym): symmetry, (asym): asymmetry (deform): deformation

2.3.4 Mechanical properties

PLA film have characteristics relatively comparable to PET and PS[44], and it has been reported to have relatively good mechanical and processing properties[21]. Semicrystalline PLLA has a tensile strength of 50-70 MPa, tensile modulus of 3000-4000 MPa, elongation at break of 2-10%, flexural strength of 100 MPa, and flexural modulus of 4000-5000 MPa[33, 45-47]. These three mechanical properties of PLLA and other biodegradable polymers are compared to with petroleum based polymers in Table 2.3.

Table 2.3 Comparison of PLLA and several biodegradable polymers with LDPE, PS, and PET, adapted from Clarinval and Halleux [48]

Polymers	Tensile strength, MPa	Tensile modulus, MPa	Elongation at break, %
LDPE	8 to 20	300 to 500	100 to 1000
PCL	4 to 8	390 to 470	700 to 1000
Starch	35 to 80	600 to 850	580 to 820
PBAT	34 to 40	-	500 to 800
PS	34 to 50	2300 to 3300	1.2 to 2.5
PLA	48 to 53	3500	30 to 240
PET	48 to 72	200 to 4100	30 to 300
PHB	25 to 40	3500	5 to 8
PVA	28 to 46	380 to 530	-

The molecular weight and percent crystallinity have a profound effect on the mechanical properties. According to Engelberg *et al.*, (1996) increasing the molecular weight from 107,000 to 550,000 Da results in a 20% increase in tensile strength[49].

Impact resistance is a critical parameter for tailoring PLA for packaging applications. It is reported that the Izod impact strength of PLLA increases as the molecular weight increases. In addition, annealed PLLA has much higher impact resistance value (32 to 66-70 J·m⁻¹) than

amorphous PLLA (19 to $26 \text{ J}\cdot\text{m}^{-1}$) indicating that the impact resistance is influenced by the crystallinity[50]. Crystallites of PLLA can act as physical cross-links, decreasing the chance for a growing crack in a specimen to propagate[51]. Anderson *et al.* reported that notched Izod impact strength of PLLA was found to be in the range of 2.0 to $2.6 \text{ kJ}\cdot\text{m}^{-2}$ [52].

The PLA processing condition has a significant effect on its impact strength. Grijpma *et al.* investigated the impact strength of PLLA with a weight average molecular weight of $780,000$ Da, and found the impact strength decrease significantly from $47 \text{ kJ}\cdot\text{m}^{-2}$ to $12 \text{ kJ}\cdot\text{m}^{-2}$ after compression molding. They demonstrated that the decrease of impact strength could be attributed to the loss of crystallinity induced by the rapid cooling rate of the process[53]. Due to PLA's low impact strength, the effect of crystallinity and molecular weight should be properly considered for packaging applications.

2.3.5 Barrier properties

One of the important properties for food and pharmaceutical packaging application is barrier properties to oxygen, carbon dioxide, and water vapor. The barrier properties of PLA have been widely investigated by many researchers. Lehermeier *et al.* reported the oxygen permeability coefficient (O_2 permeability) for PLA at $25 \text{ }^\circ\text{C}$ as $3.3 \times 10^{-17} \text{ kg}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$, and permeability coefficient of carbon dioxide (CO_2 permeability) at $25 \text{ }^\circ\text{C}$ as $1.76 \times 10^{-17} \text{ kg}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$ [54]. The author also found that polymer chain branching and small changes in L:D stereo-chemical ratio did not have an effect on barrier properties[54]. Auras *et al.* (2004) investigated the oxygen permeability coefficient of PLA under different humidity conditions and

three different temperatures. The O₂ permeability considerably increased from 3.5×10^{-18} to 11×10^{-18} kg·m·m⁻²·s⁻¹·Pa⁻¹ as the temperature increased from 5 to 40 °C[55]. The CO₂ permeability of two different PLA resins was found to be 2.77×10^{-17} kg·m·m⁻²·s⁻¹·Pa⁻¹ (2% of D-lactide) and 1.99×10^{-17} kg·m·m⁻²·s⁻¹·Pa⁻¹ (6% of D-lactide) at 25 °C and 0% RH, respectively[55]. The difference between these two films can be attributed to difference in the film morphologies. Bao *et al.* [56] found pure gas permeation properties of PLA which disagreed with those of Lehermeier's work. They applied a time-lag method for the determination of PLA permeation to pure gases, and determined diffusivity and solubility of N₂, CO₂, and O₂ of PLA film. Diffusivity and solubility of PLA with 98.7% L-lactide and 1.3% D-lactide for N₂ were found to be 2.4×10^{-8} cm²·s⁻¹, and 2.2×10^{-4} cm³·cm⁻³(polymer) cm Hg⁻¹, respectively. The permeation properties for, O₂ and CO₂ of PLA film obtained are presented in Table 2.4.

Table 2.4 O₂ and CO₂ permeation properties of PLA at 30 °C, adapted from Bao *et al.*[56]

Permeant gas	L:D ratio	<i>P</i> (Barrer)*	<i>D</i> (cm ² ·s ⁻¹)	<i>S</i> (cm ³ ·cm ⁻³ ·cmHg ⁻¹)
O ₂	98.7:1.3	1.10	4.4×10^{-9}	0.025
	80:20	0.51	3.8×10^{-9}	0.013
	50:50	0.71	4.5×10^{-9}	0.016
CO ₂	98.7:1.3	0.26	5.7×10^{-8}	4.9×10^{-4}
	80:20	0.18	5.6×10^{-8}	3.2×10^{-4}
	50:50	0.17	7.6×10^{-8}	2.2×10^{-4}

*Barrer (10^{-10} ·cm³·cm·cm⁻²·s⁻¹·cmHg⁻¹)

Shogren (1997) determined the water vapor transmission rate (WVTR) of crystalline and amorphous PLA. WVTR of crystalline PLA was found to be 27, 82, and 333 $\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ at three different temperatures, 6, 25, and 49 °C, respectively. In case of amorphous PLA, WVTR was calculated to be 54, 172, and 1100 $\text{g}\cdot\text{m}^{-2}\cdot\text{day}^{-1}$ at 6, 25, and 49 °C, respectively[57]. Siparsky *et al.* examined the water vapor permeability coefficient (H_2O permeability) of PLA, which was found to be $9.63 \times 10^{-14} \text{kg}\cdot\text{m}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$ at 20 °C and 50% RH[58].

Tsuji *et al.* (2006) [59] investigated the effects of percent crystallinity and molecular weight of PLA films on water vapor transmission rate (WVTR), and found that the WVTR of PLA films reduced monotonically with increasing crystallinity from 0 to 20%, and leveled off after exceeding 30% crystallinity. They suggested that the change could be due to the higher resistance of restricted amorphous regions to water vapor permeation as compared to that of the free amorphous regions. They also found that the molecular weight change of PLA films from 9×10^4 to $5 \times 10^5 \text{g}\cdot\text{mol}^{-1}$ has no significant effect on their WVTR values.

Since the oxygen transmission rate of a package or film is considered an important factor, especially for food products susceptible to oxidation, the relatively high values of oxygen transmission rate of PLA film can have an effect on the quality of the oxygen sensitive product. In addition, WVTR is also a key factor in the pharmaceutical packaging industry due to the water sensitivity of products. Barrier properties should be well understood for specific packaging applications.

2.3.6 Rheological properties

Melt rheological properties are useful information for understanding of thermoplastic polymer melt behavior during processing. PLA resin is currently converted into various products such as highly oriented fibers, oriented film or sheet, thermoformed containers, injection stretch blow molded bottles, and foams, using different processing techniques. Therefore, the flow characteristics of a polymer should be carefully considered to optimize effective processing conditions and predict the properties of the final products. Important factors affecting the flow characteristics of PLA include molecular weight, molecular weight distribution, degree of branching, temperature, and melt stability.

The rheological behaviors of polymer melts in the terminal region (low frequency) is typically determined by several parameters such as zero shear viscosity (η_0) and elasticity coefficient (A_G) as given in the equations below[60].

$$\eta_0 = \lim_{\omega \rightarrow 0} \eta^*(\omega) \quad (4)$$

$$A_G = \lim_{\omega \rightarrow 0} \frac{G'(\omega)}{\omega^2} \quad (5)$$

where η^* : complex viscosity(Pa · s)

G' : storage modulus (Pa)

ω : frequency (rad · s⁻¹)

In the terminal region, the storage and loss modulus as a function of frequency tend to have slopes of 2 and 1, respectively[61].

The relationship of η_o with the molecular weight of linear amorphous polymers can be expressed by the empirical equations described by Fox and Loshaek as follows:[62]

$$\eta_o = K (M_w)^a \quad (6)$$

$$A_G = K' (M_w)^b \quad (7)$$

where K and K' : constants that depend on polymer type and temperature
the power law factor a and b : the slope of $\log(\eta_o)$ versus $\log M_w$
the slope of $\log(A_G)$ versus $\log M_w$

It is well known that the molecular weight exponent, a , has been predicted theoretically to have a universal value of 3.4 above M_c , the critical molecular weight of entanglements, for linear flexible polymers[63, 64].

PLA shows pseudo-plastic non-Newtonian flow behavior like many other typical thermoplastic polymers. The rheological properties of three biodegradable aliphatic polyesters, poly(ϵ -caprolactone) (PCL), PLA, and poly(hydroxybutyrate valerate) (PHBV), were studied by Ramkumar *et al.* (1998) The rheological behaviors of PCL and PLA was typical for rheological linear polymers. G' and G'' were proportional to ω^2 and ω , respectively; in the terminal region since the polymer chains could be fully relaxed and exhibit terminal flow behavior which is a typical feature of linear polymers. It was also confirmed that PDLLA showed higher G' indicating a more elastic nature than PLLA[65]. Cooper-White and Mackay (1999) investigated the dynamic rheological properties of PLLA with molecular weights of 2,000 to 360,000 Da. PLLA melts showed power law exponents for η_o and A_G of 4.0 and 8.0 with M_w in the terminal

region. The deviation from the theoretical value of 3.4 could be attributed to steric hindrance originating from the excessive coil expansion. It is also noted that large molecular weights would be required in order to have similar melt viscoelastic properties to conventional polymers such as polystyrene[60]. Janzen and Dorgan (2010) have extensively investigated the rheological properties of PLLA melt. The η_o scale was found to be 3.4 power with M_w regardless of the optical purity of PLLA, showing good agreement with Fox and Loshaek's empirical relationship. Strain hardening during extension in the melt was observed, and this is a key factor for processes such as fiber spinning, film casting, and film blowing[64, 66-68].

2.3.7 Hydrolytic degradation

Degradation of PLA generally occurs by water uptake, which is followed by hydrolysis of the ester group in the PLA chain. The degradation rate can be affected by various factors such as optical purity, crystallinity, morphology, molecular weight, molecular weight distribution, and water permeability[69]. The PLA degradation rate during hydrolysis is mainly determined by its reactivity with water and catalysts. In general, high temperatures and humid environments result in fast degradation of PLA[30]. The PLA hydrolysis degradation process is described in Figure 2.7.

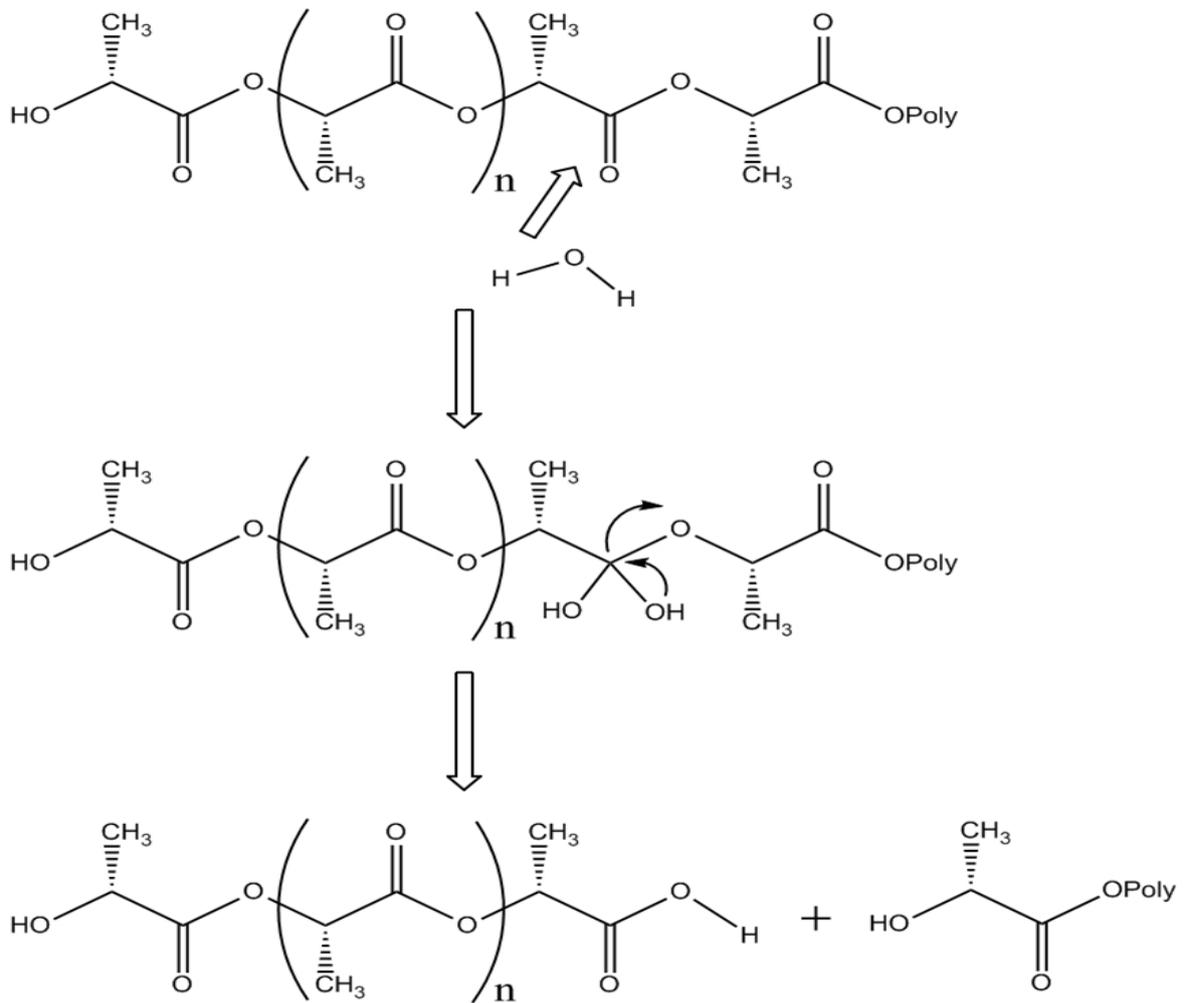


Figure 2.7 The hydrolysis process of PLA, adapted from Liu *et al.*[70]

The degradation rate of PLA is a critical factor for biomedical applications[71]. Bergsma *et al.* reported that the slow degradation rate of PLA could lead to years of *in vivo* life time of PLA[72]. In addition, this slow degradation rate can be a problem with respect to disposal of packaging items.

PLA is hydrolyzed by small amounts of presence water in the melt state, resulting in decrease in molecular weight and mechanical properties. Therefore, complete drying of PLA before processing is required[70].

2.3.8 Application and limitations of PLA

PLA was approved by the US Food and Drug Administration (US-FDA) in the 1970s for packages intended to be in contact with food[73]. PLA is currently being used as a packaging material for some short shelf life produce. Common applications also include containers, drinking cups, sundae and salad cups, overwrap and lamination films, and blister packages produced by extrusion or co-extrusion, thermoforming, and injection blow molding processes[74, 75]. Several commercial applications of PLA are listed in Table 2.5.

Table 2.5 Commercial applications of PLA, adapted from Platt and Jamshidian *et al.* [76, 77]

Application area	Product type	Manufacturer
Packaging	Film and trays for fruit, vegetable, and meat	Treophan, Natura, IPER, Sainsburys, Sulzer, Ecoproducts, RPC
	Yogurt cups	Cristallina/Cargill Dow
	Rigid transparent packaging of batteries	Panasonic
	Trays and bowls for fast food	McDonalds
	Envelopes and paper bags with transparent windows	Mitsui, Ecocard
Agriculture and horticulture	Mulching films	Novamont, Cargill Dow
Long life consumer good	T-shirts and socks	FILA/Cargill Dow, Kanebo Gosen
	Blankets	Ingeo
	Casing of walkman	Sony
	Compact disks	Sanyo Marvic Media/Lacea
	Computer keys	Fujitsu
	Small components of laptop	Fujitsu/Lacea
	Wheel covers	Toyota

PLA has several disadvantages for specific packaging applications. PLA is very brittle with less than 10% elongation at break[78, 79]. Although its tensile strength and elastic modulus are comparable to PET[30], the poor toughness limits its use in industrial applications. Many researchers are currently trying to improve this brittle nature of PLA. It has recently been reported that functional modifications of PLA may have a significant potential to improve the mechanical properties of PLA in addition to providing controlled release of compounds such as antimicrobials, antioxidants, and bioactive compounds[80].

2.4 Starch

Starches are naturally occurring materials present as water insoluble granules that can be found in plant roots, tubers, seeds or grains. The starch granule is basically composed of two main polysaccharides, amylose and amylopectin, and lipids and proteins. The starch properties are highly dependent on granule shapes, sizes, and amylose content, and these factors should be considered for starch based processing.

There are several types of starch, and each starch normally has different granule size, size distributions, granule structure, and degree of amylose and amylopectin branching in the starch structure[81]. The chemical structure of starch is presented in Figure 2.8.

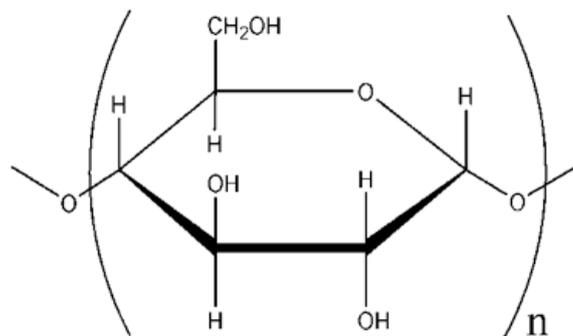


Figure 2.8 Chemical structure of Starch

Amylose has a linear molecular structure composed of 1,4-linked α -D-glucopyranosyl units and slightly branched 1,6-linked α -linkage. The typical molecular weight of amylose is known to be in the range of $10^5 \sim 10^6$ Da[81-83]. Unlike amylose, amylopectin has a highly branched molecular structure composed of residual α -D-glucopyranosyl units and 1,4-linkage having 1,6-linkage in branching site. The molecular weight is in the range of $10^6 \sim 10^8$ Da[81, 84]. Starch crystallizes in three types of structures; A, B, and C types. The A type is found in cereal starches such as maize, wheat, and rice. The B type is found in tuber starches such as potato and sago, and the C type is intermediate between the A and B type and is found in bean and other root starches[85].

Starch is a biodegradable material. It has the advantages of being from renewable resources, biodegradable, abundantly available and cost effective[86, 87]. However, starch has limitations for packaging applications such as poor mechanical properties, (*i.e.*, brittleness) and its hydrophilic nature. Therefore, the extensive research has been carried out in order to modify starch and improve its physical properties[86].

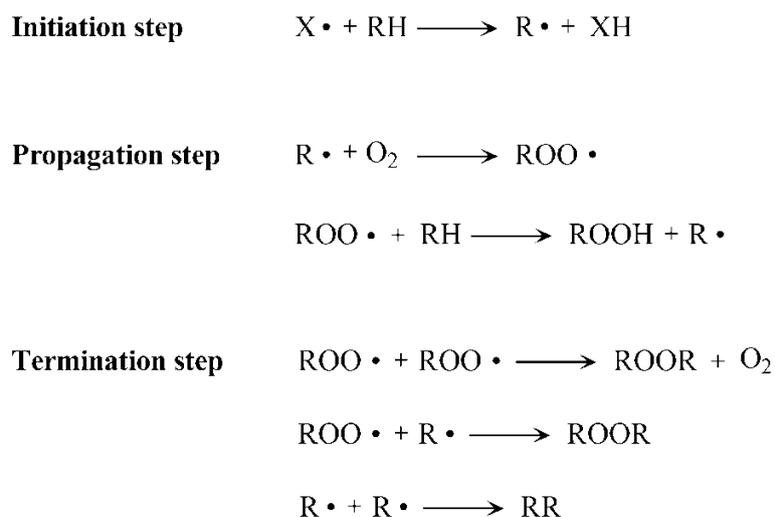
Blending starch with biodegradable polymers is one approach in order to obtain a material with a wide range of mechanical properties without losing its biodegradability[88, 89]. Noomhorm *et al.* (2006) found that addition of 10 wt.-% of polydioxolane (PDXL) made PDXL partially adhere to tapioca starch (TS) surface to facilitate the production of a miscible blend.[90] Thermoplastic starch (TPS) has also been widely used to develop blends with various biodegradable polymers. Narayan *et al.* (2006) investigated the physical properties of blown films made from TPS chemically modified with maleic acid, and grafted to EcoflexTM, poly (butylene adipate-co-terephthalate) (PBAT), using a free radical initiator[91]. It was reported that

all blend compositions showed relatively good elongation at break comparable to EcoflexTM.

However, lower tensile strength and lower modulus were also found. Addition of 4 wt.-% clays to chemically modified TPS/EcoflexTM graft copolymer enhanced the tensile strength and elongation at break, which were reported relatively higher than LDPE.

2.5 Lipid autoxidation

Lipid autoxidation in foods decreases the shelf life of foods such as cereals, cookies, and vegetable oils. Although food products may be hermetically sealed when they are packaged, both oxidative and non-oxidative degradation during storage or transportation takes place[92]. Miller *et al.* (1997) reported that fatty foods even with less than 1% lipids could be affected by chemical oxidation[93]. Lipid autoxidation is a spontaneous reaction between oxygen and lipids. It is the most common lipid oxidative reaction resulting in oxidative deterioration, and generally shows an induction period (IP)[94]. The induction period is the time during which the lipid deterioration is initiated and proceeds very slow. The oxidative deterioration of the lipids occurs very fast after the IP ends[94]. Three steps are involved in the autoxidation process; initiation, propagation, and chain termination. (Scheme 2.1) Lipid radicals are formed from lipid molecules during the initiation step. Production of radicals occurs by metal catalyst, light and so on. After that, a propagation reaction follows resulting in the formation of peroxy radicals (ROO \cdot). These peroxy radicals are converted into lipid hydroperoxides (ROOH) and alkyl radicals (R \cdot) from the reaction between the peroxy radicals and lipid molecules. Finally, the free radicals are combined to form peroxide molecules during the termination step[94].



Scheme 2.1 Lipid autoxidation reaction [94]

2.6 Antioxidants

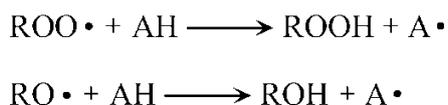
To minimize lipid autoxidation, the use of antioxidants added into the food products could be considered, and consequently extend the shelf life of the product. In the past, large amounts of antioxidants were directly added into the foods, which were rapidly depleted. In the last few decades, polymer-packaging systems have been designed to deliver antioxidants in a controlled manner. This system provides several benefits such as controlled release of the compound, protection of the product where is most needed, especially on the surface, and limited amounts of antioxidant added to the food product.

There are various types of antioxidants; some are synthetics and others naturally occur in plants. Natural antioxidants include carotenoids, vitamins, phenols, flavonoids, dietary glutathionine, and so on [95], while synthetic antioxidants include gallates, BHT, BHA, and others[94]. Although the synthetic antioxidants are approved as food additives and generally considered as safe, their use is limited to about $200 \text{ mg} \cdot \text{kg}^{-1}$ food as regulated by US Food and Drug Administration (FDA) and some other European agencies[96]. In general consumers prefer

to avoid synthetic antioxidants and prefer the use of natural antioxidants.

Antioxidants can be classified into two groups based on their mode of action: preventing the formation of free radical in the initiation step, or stopping the propagation of free radical chains[94]. The phenolic compounds such as vitamin E belong to the antioxidants that inhibit the formation of free radicals. Vitamin E is also used as a polymer stabilizer such as IrgafosTM and IrganoxTM to stabilize during the processing of packaging materials especially polyolefin.

Vitamin E, however, is unstable at high temperatures, so BHT is frequently used to prevent oxidation of food subjected to high temperatures. The antioxidants that prevent the propagation of free radical chains retard oxidation by binding the metal ions, scavenging oxygen, changing hydroperoxides into non-radical species, absorbing UV radiation or deactivating singlet oxygen[94]. Antioxidants also have been used as peroxide decomposers[95]. The general mode of antioxidant reaction is given in Scheme 2.2. The antioxidants (AH) interrupt the propagation step of the free radicals by scavenging them (ROO• and RO•), and form the antioxidant radical A•, which has a low activity resulting in no further oxidation reaction[97].



Scheme 2.2 Radical scavenging antioxidant reactions, adapted from Gordon *et al.*[94]

2.6.1 α -Tocopherol

α -Tocopherol (α -TOC) is one of four tocopherols having antioxidant activity, and it is the most abundant form in nature. It is a natural antioxidant presents in grains like soybeans, cottonseed, and sunflowers and its chemical structure is presented in Figure 2.9.

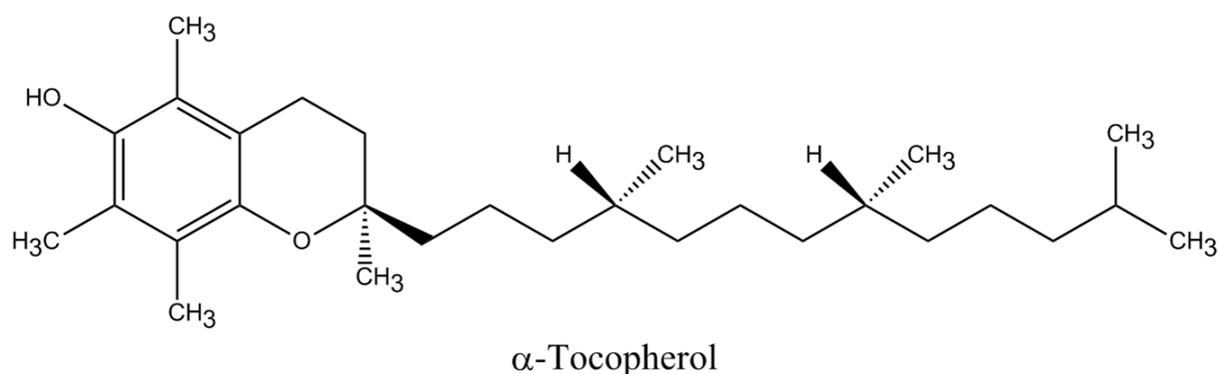


Figure 2.9 Chemical structure of α -TOC

α -TOC is widely known to be effective in preventing lipid peroxidation and other radical oxidative reaction[98-100]. α -TOC antioxidant activity has been extensively investigated due to its ability to prevent chronic diseases such as cardiovascular diseases, atherosclerosis, and cancer. Stampfer *et al.* (1993) reported that the intake of vitamin E rather than vitamin C was correlated with a reduced risk of cardiovascular disease, indicating that vitamin E has an effective function as an antioxidant[101]. Vitamin E functions as a chain-breaking antioxidant, preventing the free radical propagation reaction[98, 102]. Natural α -TOC has a higher antioxidant capability as compared to synthetic racemic α -TOC since it is selectively recognized by the α -TOC transfer protein[103].

Since α -TOC is well known as a safe additive, there is no restriction to its use in food products. Therefore, the applications of α -TOC in food have increased[104]. It is also used as an additive during the processing of packaging materials[105-107]. Mallécol *et al.* (2001) reported that vitamin E effectively delayed the oxidation of high density poly(ethylene) (HDPE) during γ -irradiation[108]. Min *et al.* (2002) found that singlet oxygen oxidation produced undesirable compounds in foods during processing and storage, and carotenoids and tocopherols in foods could minimize singlet oxygen oxidation[109]. Wessling *et al.* (2000) reported that the addition

of above 360 ppm of α -TOC in LDPE delayed the oxidation of linoleic acid at 6 °C. In addition, they also suggested possible change in the mechanical properties, color, and the oxygen permeability of LDPE film when α -TOC is added[110].

2.6.2 Resveratrol

Resveratrol is a polyphenolic compound, which is a natural antioxidant mainly present in grapes[111], grape juice[112], wine[113], peanuts[114] and a number of other plant species [115]. Resveratrol has a relatively good thermal stability with a melting temperature of 253 ~ 255 °C. The chemical structure of resveratrol is provided in Figure 2.10.

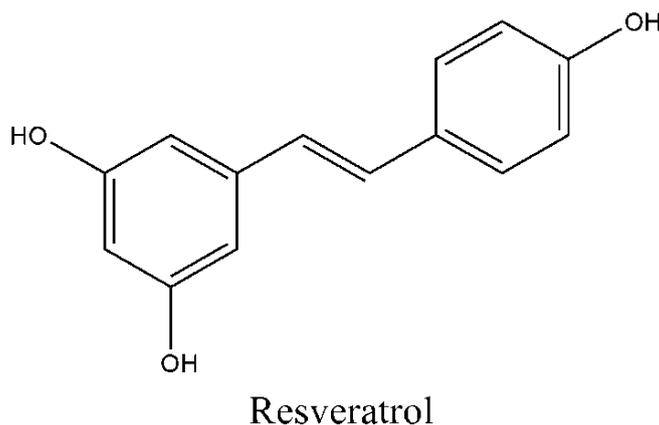


Figure 2.10 Chemical structure of resveratrol

Resveratrol was initially studied as a cancer chemopreventive agent by Saiko *et al.*(2008) [116] and Delmas *et al.*(2006) [117] It has been reported that the hydroxylated structure of resveratrol enables a radical derivative stabilized chemical form by the delocalization of two electrons between the two aromatic cycles and the methylene bridge[118]. Sale *et al.* (2004) reported that a small dose of dietary resveratrol could reduce colon carcinogenesis in rats and

mice[119]. Recently resveratrol has gained attraction in the food area as a powerful antioxidant[120]. Several studies reported that resveratrol could be used as a preventive agent of several important pathologies such as neurodegenerative processes, viral infections, vascular diseases, and cancers[117, 118].

The two aromatic rings in resveratrol have high free radical-scavenging capacity than propyl gallate, ascorbic acid and α -TOC[121]. Although resveratrol has great potential to be used as a food antioxidant, dietary and supplement recommendation and complete understanding of metabolic assimilation would be required due to its potential toxicity and human health effects. Mielink *et al.* (2006) found that the efficiency of grape seed extracts increased with increasing antioxidant concentration from 0.4 to 1.6 g kg⁻¹, suggesting potential application of resveratrol to active packaging[122]. Delmas *et al.* (2011) have recently suggested that resveratrol uptake, metabolism, and stability of the parent molecule could have an effect on the biological effects of resveratrol. They reported that resveratrol stability could involve redox reactions and biotransformation, which influences its antioxidant properties[123].

2.7 Polymer blends

Polymer blends have gained importance for many years since the blending of two polymers may give rise to a new polymeric material with enhanced properties[124, 125]. Most of the polymer blends are found to be immiscible systems and show poor mechanical properties because they greatly depend on the compatibility among the polymers, and their interfacial tension hinders the formation of coalescence during melt mixing resulting in poor interfacial adhesion[125]. These immiscible blends are characterized by a two-phase morphology, poor physical and chemical interactions across the phase boundaries and poor mechanical properties[126, 127]. Blends could

provide cost saving as compared to developing new polymers systems[128, 129]. The addition of block or graft copolymer to the blend has been a common strategy to enhance the compatibility among polymers and develop an interfacial adhesion between the two polymers. However, the molecular weight of the polymers used in blends is an important factor that should be considered, and there are cost problems generated by the preparation of copolymers for special applications[130-132].

Blending with petroleum based polymers has been widely studied to improve the mechanical properties of PLA. Wang *et al.* (2001) investigated PLA/LDPE blends, and reported that the crystallinity of PLA had a significant effect on the toughness of the blends[133]. Anderson *et al.* (2003) reported that amorphous PLA/LLDPE blends with a PLLA–LDPE block copolymer as a compatibilizer improved the toughness of the blend while semi-crystalline PLLA/LLDPE blends showed enhanced toughness without a compatibilizer. The semi-crystalline PLLA showed significantly better adhesion to the LLDPE than amorphous PLA. This could be related to the improvement of adhesion between the PLLA and LDPE[134]. Gajria *et al.* (1996) studied PLA/poly(vinyl acetate) (PVA) blends, and found that the tensile strength of the blend improved with 5 to 30 wt.-% of PVA. The elongation at break also improved with an addition of 5 wt.-% of PVA[135]. Zhang *et al.* (2003) investigated blends of amorphous poly(DL-lactide) (PDLLA) and crystalline poly(L-lactide) (PLLA) with poly(methyl methacrylate) (PMMA). Miscible PDLLA/PMMA blends were found by using solution/precipitation method while the blends showed partially miscible behavior with a chloroform solution casting method[136]. PLA/Poly(vinyl alcohol) (PVOH) blends have also been widely used in biomedical and membrane technology. Jawalkar *et al.* (2006) reported that blends were miscible above 25 wt.-% PLLA, while other compositions of blends were

immiscible. They also suggested that the miscibility of PLA and PVOH could be attributed to the hydrogen-bonding effects[137].

PLA blends with other biodegradable polymers have been also extensively studied to improve mechanical properties without compromising the biodegradability. Poly(3-hydroxybutyrate)-co-(3-hydroxyvalerate) (PHBV) was blended with PLA by a solvent casting method. The blends showed partial molecular interaction between PLA and PHBV, but phase separation was found indicating that the blends were not compatible[138]. Takagi *et al.* (2004) found improvement in toughness when using PLA/poly(3-hydroxyalkanoate) (PHA) blends. The addition of epoxy groups into PHA made the epoxy group combine with the hydroxyl group of PLA resulting in increasing interaction between the phases[139]. Wang *et al.* (2003) blended PLA with starch by melt blending, and the toughness of the blends decreased with the physical aging of samples that were stored for 12 months at 25 °C and 50 % relative humidity. The reduction of toughness was caused by the reduction of the compatibility between the two phases of PLA and starch during aging[140].

PCL has been extensively investigated for producing blends with PLA due to PCL is ductility. Tsuji *et al.* (2003) prepared a copolymer of L-lactide and ϵ -caprolactone (PLLA-CL) as a compatibilizer, and added it to PLLA/PCL blends. They suggested that the addition of PLLA-CL in the blends increased the compatibility between the PLLA and PCL phases[141]. It was reported that the addition of ethylene oxide and propylene oxide surfactant significantly improved the toughness of PLLA/PDLLA blends, and increased elongation at break in PLLA/PCL blends[142]. Semba *et al.* (2006) investigated the effect of crosslinking dicumyl peroxide (DCP) on PLA/PCL blends, and they found that blends with 0.2 phr DCP showed high compatibility due to increased interfacial adhesion between PLA and PCL. The optimum blend

ratio of PLA/PCL was found to be 70/30, and the tensile strength and modulus were intermediate between neat PLA and neat PCL[143]. Lin *et al.* (2007) blended PLA with hyperbranched poly(ester amide) (HBP) to increase the toughness of PLA. The elongation at break of the blends was improved more than 10 times as compared to neat PLA with 20 wt.-% of HBP, and hydrogen bonding between the carbonyl group of PLA with the hydroxyl group and amine group of HBP was found to be responsible for increasing the yield strength of the blend[144]. Takayama *et al.* (2006) introduced lysine triisocyanate (LTI) as an additive to be used in the PLA/PCL blends. They found that the compatibility of PLA/PCL was improved with addition of LTI resulting in the reduction of spherulite size of the PCL. It was suggested that this behavior could reduce the interfacial tension and promote a blended system, consequently increasing the toughness of the PLA/PCL blends[145].

Suyatma *et al.* (2004) investigated PLA/chitosan blends prepared by solution casting. Phase separation was found, creating an incompatible blend. However, they reported that blending chitosan with PLA could enhance the water vapor barrier and hydrophobicity of the chitosan[146]. Ke *et al.* (2003) reported that starch containing above 50% amylose content improved the water resistance without compromising mechanical properties when used for blending with PLA. It seems that the water absorption of the PLA/starch blends was affected by amylose content[147]. They also investigated the crystallization behavior of PLA/starch blends, and found that 1% starch effectively increased the crystallization rate[148]. Table 2.5 summarizes several PLA blends studied for packaging applications

Table 2.6 Summary of PLA blends for packaging applications

Polymers	Properties	References
Polyvinyl acetate	Increase of tensile strength and percent elongation	Gajria <i>et al.</i> [135]
Poly ethylene oxide	Elongation at break of more than 500%	Nijenhuis <i>et al.</i> [149]
Poly ϵ -caprolactone	Improvement of mechanical properties	Tsuji <i>et al.</i> [150]
Poly ethylene glycol	Enhance the crystallinity of PLA and biodegradability	Sheth <i>et al.</i> [151]
Starch with different plasticizers	Lowering the price, decreasing T_g , and increasing crystallinity and biodegradability	Ke <i>et al.</i> [152], Jacobsen <i>et al.</i> [153], Ke <i>et al.</i> [147]
Polyvinyl alcohol and starch	Increase of tensile strength	Ke <i>et al.</i> [154]
Ethylene vinyl alcohol	Enhancement of mechanical, thermal, and biodegradable properties	Lee <i>et al.</i> [155]
Poly ethylene glycidyl methacrylate	Super-tough PLA	Oyama [156]

2.8 Reactive compatibilization

Reactive compatibilization is one of the methods to improve compatibility of blends by conducting a chemical reaction of both polymers while blending, in this way generating reactive sites at the interface of both polymers, facilitating interaction between the polymers[125, 128, 129]. It is well known that the polymers with -OH, -COOH and/or -NH₂ groups can be chemically coupled with reactive polymers such as maleic anhydride[157, 158], oxazoline[159, 160], and epoxide[161-163]. The compatibilizer formed by chemical reactions between polymer chains that are mutually reactive is called ‘*In-situ formed compatibilizer.*’ During the compatibilization process, small-dispersed phases (or domains) are formed, and they could enhance the interfacial adhesion of two immiscible polymers by reducing the interfacial tension between the two polymers. The phase morphology of blends can be stabilized by preventing the coalescence of dispersed domains resulting in bigger domains affecting the phase separation

behaviors of blend systems. Improved mechanical properties of the polymer blends can be accomplished with more energy transferred across one phase to the other at the interface of the two polymers[128, 129].

Maleic anhydride (MAH) is one of the most widely used reactive compatibilizers due to its good chemical reactivity. It also has low toxicity and low potential to polymerize itself under free radical grafting conditions.[164] Many researchers have reported that MAH can be easily grafted onto polyolefins in the presence of an initiator during melt processing[165-168]. Gaylord *et al.* (1982, 1983, and 1988) reported the formation of single and oligomeric grafts by grafting of MAH onto polyolefins, and proposed that a bridge could be formed between grafted MAH and the polymer chains[165, 167, 168]. The MAH can functionalize both PLA and starch since PLA contains carboxyl and hydroxyl end groups as functional groups, and starch has hydroxyl groups as its functional groups[169].

The chemical reaction between PLA, starch, and MAH described by Zhang *et al.* [170] is provided in Figure 2.11.

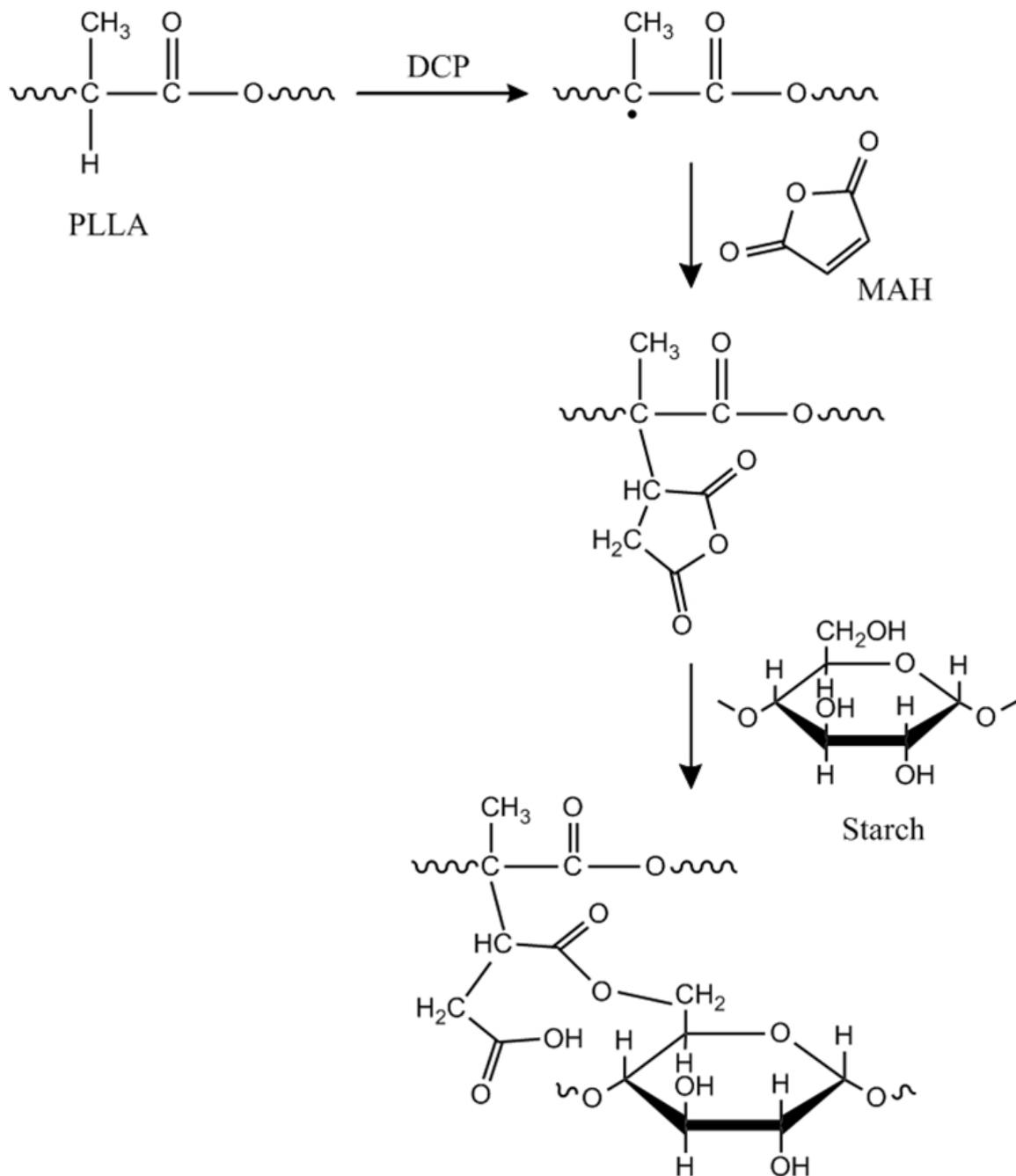


Figure 2.11 Reaction of PLLA, MAH, and Starch, adapted from Zhang *et al.*[170]

Passaglia *et al.* (2003) reported MAH and diethylmaleate (DEM) have increased the efficiency of the functionalization ability of ethylene/propylene copolymer under the dicumyl peroxide (DCP)

selected as a free radical initiator[171]. There are several peroxide initiators for grafting PLA or starch such as 2,5-bis((tert-butylperoxy)-2,5-dimethyl hexane (Luperox® 101) or 2,5-dimethyl hexane-2,5-di-(tert-butylperoxy)hexane (Lupersol L101), DCP, and benzoyl peroxide (BP). They are commonly applied for indirect additives used in food contact substances[172-174].

2.9 Migration

The term migration is normally used to express the process of mass transfer from packaging materials into packaged product especially when the product is liquid or semiliquid[175].

Migration is important in the food and pharmaceutical packaging industry since it can impact the organoleptic and toxicity properties of food products, and has a profound effect on the final quality of packaged products. For this reason, the migration has become a critical factor in food and pharmaceutical legislation in many countries[176]. There are two types of packaging migration that are widely accepted, *global migration* and *specific migration*. *Global migration* is the total amount of migrants transferred from a package sample to a food regardless of the composition with units of mass per sample mass or mass per contact area between food and packaging material. Global migration analysis can be performed by exposing a plastic film or package to recommended simulant and specific time-temperature conditions. The plastic film or package is removed from the migration cell and the liquid simulant is completely evaporated. The dried residue weight is the value for global migration, but there is no theoretical prediction of this value because each migrant is transported with different sorption and diffusion coefficients. *Specific migration* is the amount of a specific migrant transferred to a food, and it focuses on substances that are potentially toxic to human, and it is only controlled in case such substances are present in food products. Specific migration analysis can be carried out with

several different procedures. The migrant properties, especially its volatility and compatibility with the food phase, will determine the best procedures for analysis. The total amount of specific migration of a substance can be determined after exposing the material to the simulant, and the migrant is analyzed directly from the simulant or from the headspace by gas or liquid chromatography or by residual migrant in the package[55, 176].

In addition to global and specific migration, it is valuable to assess the *potential migration*. The potential migration is defined as the total amount of a specific migrant extractable from the package. The value of the potential migration is always higher than that of specific migration regardless of the simulant types or food-package system. If the value from potential migration is below the limits given in regulations, no further analysis is required and the packaging materials can be considered acceptable for food contact[177]. Generally, migration studies are performed with food simulants such as water, vegetable oil, aqueous ethanol, and some real foods under specific temperature and time conditions. There is extensive information about migration in the literature[178-180].

The U. S. Food and Drug Administrations (USFDA) defines a Food Contact Substance (FCS) as "Any substance that is intended for use as a component of materials used in manufacturing, packing, packaging, transporting, or holding food if the use is not intended to have any technical effect on the food"[180] The USFDA recommends to assess the level of the FCS in the food contact articles to determine the concentration of FCS in the daily diet. The level of the FCS concentration can be determined by total migration experiments where total migration is defined as the total amount of FCS or migrant transferred from a package sample (gram per sample gram) to a food regardless of composition. Guidance for migration experiments can be found in ASTM D 4754-98 (2003)[181]. In addition, the USFDA

recommends the use of food simulants for the migration experiment as shown in Table 2.7.

Table 2.7 Food simulants recommended from USFDA

Food-Type	Simulant
Aqueous & Acidic Foods (Food Types I, II, IVB, VIB, and VIIB)	10% Ethanol
Low- and High-alcoholic Foods (Food Types VIA, VIC)	10 or 50% Ethanol
Fatty Foods (Food Types III, IVA, V, VIIA, IX)	Food oil (e.g., Corn oil), HB307, or Miglyol 812

Migration is a combined phenomenon of thermodynamic equilibrium (i.e., solubility or partition coefficient of the migrant compound) and kinetics of mass transfer (i.e., diffusion coefficients). Therefore, it is critical to control both the partition coefficient and diffusion coefficient of the migrant in package-food simulant systems[55].

The one dimensional diffusion solution equations of the Fick's second law for migrants from the plastic films or package to a limited volume solution (simulant) is used to determine the diffusion coefficient (D) (1) and (4)[182]:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} \exp\left\{-Dq_n^2 t / l^2\right\} \quad (1)$$

where l is thickness of the plastic film or package

q_n are the non zero positive roots of $\tan q_n = -\alpha q_n$, and α is expressed as

$$\alpha = \frac{V_S}{V_P \cdot K_{P,S}} \quad (2)$$

where V_S and V_P are molar volume of simulant and the plastic film or package

$K_{P,S}$ is the partition coefficient of migrants between plastic film or package and the simulant

The partition coefficient can be assumed in contact for low concentrations and calculated from the ratio of the concentration of migrants in plastic films or package ($C_{P,\infty}$) and the simulant

($C_{S,\infty}$) at equilibrium according to the following Equation (3)

$$K_{P,S} = \frac{C_{P,\infty}}{C_{S,\infty}} \quad (3)$$

Fick's second law diffusion relationship (4) shown below is applied to determine the diffusion coefficient (D) if the amount of solvent (simulant) can be considered infinite (i.e., $\alpha \gg 1$ since $V_S \gg V_P$ and/or $K_{P,S} < 1$), Equation (2) can be simplified as:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp\left\{-D(2m+1)^2 \pi^2 t / l^2\right\} \quad (4)$$

where l is thickness of the plastic film or package

The mass of migrants diffused at time t , divided by the mass of migrants diffused at equilibrium (M_t/M_∞) is plotted as a function of the square root of time t ($\text{sec}^{1/2}$) and the diffusion coefficients (D) are determined.

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CHAPTER III

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CHAPTER III

Poly(L-lactic acid) with Added α -Tocopherol and Resveratrol.

Optical, Physical, Thermal and Mechanical Properties

Abstract

Poly(L-lactic acid) (PLLA) films containing various concentrations of two natural antioxidants, α -tocopherol (α -TOC) and resveratrol, were fabricated by a melt compounding and compression molding process. The influence of the antioxidants on the optical properties such as color and UV-VIS light transmission was analyzed. The thermal, mechanical, rheological, and physical properties of PLLA films with added antioxidants were assessed. PLLA films with added α -TOC and resveratrol showed a yellowish brown color and the lightness was influenced by the presence of the antioxidants. The glass transition and melting temperatures were significantly reduced with the addition of antioxidants while enhanced thermal stability was observed, which could be a benefit and important for processing and production. PLLA films with added antioxidants were slightly more hydrophobic than neat PLLA. The combination effect of plasticizing and enhancement of the elastic modulus with differing concentrations of two antioxidants played a critical role in the mechanical and thermo-mechanical properties of PLLA films. The melt viscosity of the PLLA films added with antioxidants was substantially higher than that of neat PLLA. The higher melt viscosity and $G'(\omega)$ could be an indication of formation of entanglement between PLLA and both antioxidants.

3.1 Introduction

Commercial poly(lactic acid) (PLA) is a biobased polymer, and it is compostable[1]. PLA is generally manufactured by ring-opening polymerization of lactide as monomer. Lactide is the cyclic dimer prepared by the controlled depolymerization of lactic acid obtained by the fermentation of corn, sugar cane, or sugar beets[2, 3]. PLA is used in medical implants, sutures, and drug-delivery systems, as well as in single-use disposable items due to its good mechanical properties, thermal plasticity, and biocompatibility.[1] PLA is approved by the US Food and Drug Administration (FDA) as a food contact substance (FCS)[4, 5], and it is currently being used as packaging material for some short shelf life products. Some other applications are drinking cups, sundae and salad cups, overwrap and lamination films, and also blister packages produced through co-extrusion, thermoforming, and injection blow molding processes[6, 7].

α -Tocopherol (α -TOC) is a natural antioxidant present in grains like soybean, cottonseed, and sunflower and generally recognized as safe (GRAS) by the US FDA. There is no restriction for use of α -TOC in food products and/or as a polymer additive in functional membranes[8, 9]. Resveratrol, currently under FDA review as a dietary supplement, is also a natural antioxidant mainly present in grapes[10] and grape juice[11]. Resveratrol has relatively good thermal stability with a melting temperature of 253 ~ 255 °C. The two aromatic rings in resveratrol showed a higher radical-scavenging capacity than propyl gallate, ascorbic acid, and α -TOC[12].

Functional membranes have been found to be promising systems for the sustained release of antioxidants in food, pharmaceutical, and medical applications. Miltz *et al.* reported that when a high concentration of butylated hydroxytoluene (BHT) was imbedded in HDPE film used to package oatmeal cereal, the shelf life of the final product was extended when compared to cereal packaged in HDPE film with a low concentration of BHT.[13] Wessling *et al.* reported that the

addition of above 360 ppm of α -TOC in LDPE significantly delayed the oxidation of linoleic acid at 6 °C[14].

Since PLA is biocompatible and readily biodegradable, it could be a promising candidate as a functional membrane. For antioxidant, the main concern is to determine if the presence of the antioxidants in the film affects the film performance. Therefore, the goal of this study was to evaluate the performance of the PLA films when two antioxidants, α -TOC and resveratrol, were added to the film to obtain PLA films with sustained release of antioxidants. In order to evaluate the performance of the film, the optical, physical, thermal and mechanical properties of PLA films were assessed over a range of different concentrations of added α -TOC and resveratrol.

3.2 Experimental

3.2.1 Materials

Poly(94% L-lactic acid), PLLA (4042D), resin was provided by NatureWorks LLC, Minnetonka, MN. α -TOC (97+ % pure) and resveratrol (99% pure) were purchased from Alfa Aesar (Ward Hill, MA, USA) and ChromaDex Inc. (Santa Ana, CA, USA), respectively. The chemical structures of α -TOC and resveratrol are provided in Figure 3.1.

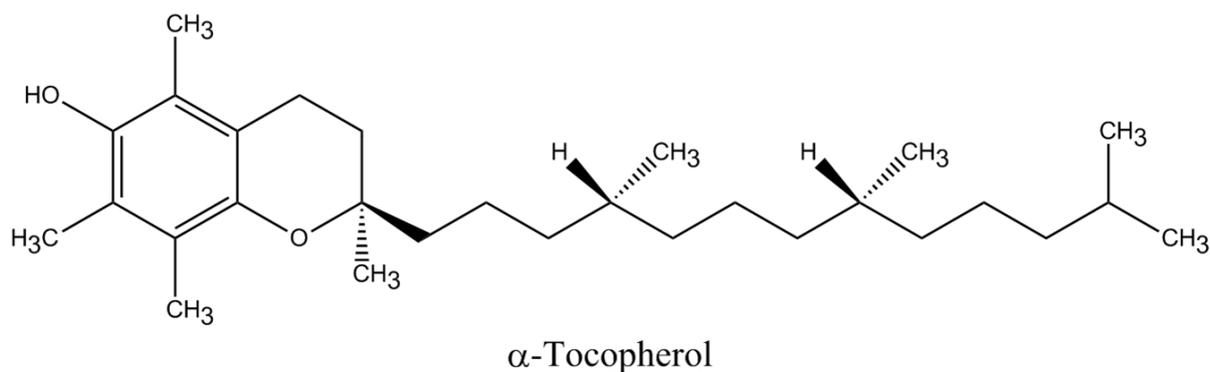
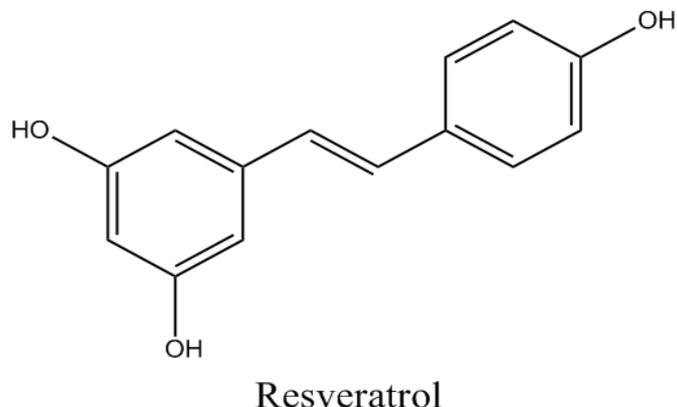


Figure 3.1 Chemical structures of α -Tocopherol and Resveratrol

Figure 3.1 (cont'd)



3.2.2 Film preparation

PLLA resin with various concentrations of both α -TOC and resveratrol were prepared by mixing them simultaneously in a Plasti-Corder[®] Rheometer equipped with a three-piece mixing head (Brabender, Duisburg, Germany). The mixing was performed at 190 °C with 60 rpm rotor speed. The concentrations of antioxidants mixed with PLLA are listed in Table 3.1. The PLLA/antioxidant mixtures were cooled to room temperature and then compression molded to films with thicknesses of 150 ~ 200 μm by a hydraulic laboratory press model 3925 (Carver, Wabash, IN) at 200 °C. All samples were kept at refrigerated conditions (-15 °C) to prevent possible migration of antioxidants from the samples before testing.

Table 3.1 Composition of PLLA/antioxidant films

Sample	α -TOC ($\text{mg}\cdot\text{g}^{-1}$ resin)	Resveratrol ($\text{mg}\cdot\text{g}^{-1}$ resin)
T1R4	10	40
T2R3	20	30
T2R2	25	25
T3R2	30	20
T4R1	40	10

3.2.3 Characterizations

3.2.3.1 Optical properties

The total color difference (ΔE^*) of the PLLA films was determined as described by the Commission Internationale de l'Eclairage (CIE) $L^*a^*b^*$ color scale with a spectro-colorimeter (JS555, Color Techno System Corporation, Tokyo, Japan). Ultraviolet–visible (UV-VIS) light transmission was measured with a UV-VIS spectrophotometer (Evolution 600, Thermo Scientific, Waltham, MA, USA) in the range of 200 ~ 800 nm at an intelli-scan speed mode and data interval of 0.5 nm. Five samples were tested for each specimen.

3.2.3.2 Contact angle and surface energy determination

Static water and methylene iodide (CH_2I_2) contact angles were measured at 23 °C using a customized static contact angle analyzer connected to a digital microscope (Dino-light, Hsinchu, Taiwan) located in a bench top vibration isolation system with stabilizer technology (Newport, Irvine, CA). A constant sessile droplet volume (100 μL) of water and CH_2I_2 were used and delivered to the surface of each film sample by a syringe needle with a pump. Five samples were tested for each specimen. The surface free energy was determined by using the Harmonic mean equations[15, 16].

$$(1 + \cos \theta_1) \gamma_1 = 4 \left(\gamma_1^d \gamma_s^d / (\gamma_1^d + \gamma_s^d) + \gamma_1^p \gamma_s^p / (\gamma_1^p + \gamma_s^p) \right) \quad (1)$$

$$(1 + \cos \theta_2) \gamma_2 = 4 \left(\gamma_2^d \gamma_s^d / (\gamma_2^d + \gamma_s^d) + \gamma_2^p \gamma_s^p / (\gamma_2^p + \gamma_s^p) \right) \quad (2)$$

where γ^d : the dispersive component

γ^p : the polar component

γ_s : solid surface energy

θ_1 : the contact angle to water

θ_2 : the contact angle to CH₂I₂

For water, $\gamma_1 = 72.8 \text{ mJ/m}^2$, $\gamma_1^d = 22.1 \text{ mJ/m}^2$, and $\gamma_1^p = 50.7 \text{ mJ/m}^2$

For CH₂I₂, $\gamma_2 = 50.8 \text{ mJ/m}^2$, $\gamma_2^d = 44.1 \text{ mJ/m}^2$, and $\gamma_2^p = 6.7 \text{ mJ/m}^2$ [13,14]

3.2.3.3 Atomic force microscopy (AFM) measurements

AFM measurements were carried out to observe the surface topography of the PLLA/antioxidant films. The scanning probe microscope (NanoScope IIIa Multimode, Digital Instrument, USA) was operated in tapping mode. The images were collected at a fixed scan rate of 2.977 Hz with scan size of 10 μm and sampling rate of 256 samples/line.

3.2.3.4 Thermal properties

The glass transition temperature (T_g), melting temperature (T_m), and percent crystallinity (X_c) were obtained with a differential scanning calorimeter (DSC) (Diamond™ DSC, Perkin-Elmer, Waltham, MA, USA). The measurements were carried out under nitrogen atmosphere with a temperature range from 20 to 220 °C at a heating rate of 10 °C/min, and were analyzed by Diamond Analysis software. The percent crystallinity was determined by Eq. (3) [17].

$$X_c (\%) = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^c (1 - x)} \times 100 \quad (3)$$

where ΔH_m is enthalpy of fusion, ΔH_c is the enthalpy of cold crystallization, ΔH_m^c is enthalpy of fusion of pure crystalline PLA; $\Delta H_m^c = 93.1$ J/g[17], x is the fraction of antioxidant.

A thermo-gravimetric analyzer (TGA Q600, TA instruments, New Castle, DE) was used to measure the change of sample weight when the samples were exposed up to 800 °C with a rate of 10 °C/min under nitrogen atmosphere with a flow rate of 20 cm³.

3.2.3.5 Thermo mechanical properties

Dynamic mechanical analysis (DMA) of the PLLA/antioxidant films was performed on a TTDMA from Triton Technology Ltd., Keyworth, UK. Samples with a width of 6.0 – 6.5 mm and a length of 12 -15 mm were cut for testing in tension mode. The sample dimensions were carefully measured and the mean values of 6 points were input. The measurement was carried out at a heating rate of 5 °C/min and a temperature range from 0 to 160 °C with a frequency of 1 Hz. The storage modulus (G') was measured for each sample in this temperature range.

3.2.3.6 Mechanical properties

Tensile strength, Young's modulus, and elongation at break were assessed by a Universal Test Machine (UTM) (Instron 4465, Instron, Canton, MA) according to ASTM D 882-02. Samples were cut into strips with dimensions of 2.54 x 15.24 cm (1 × 6 in) and conditioned at 23 °C and

50 % RH for 24 h before testing. The specimens were tested at a crosshead speed of 10 mm/min with 5.08 cm (2 in) initial gap separation.

3.2.3.7 Rheological properties

The rheological properties of neat PLLA and PLLA/antioxidant films were measured using a rotational rheometer (Haake Mars, Thermo Scientific, Newington, NH) using a 60 mm parallel plate. All the samples were vacuum dried at 60°C for 24 hr before testing. Tests were performed at 190°C under a nitrogen atmosphere to avoid degradation. A dynamic frequency sweep test over a frequency range of 0.1 ~ 100 rad⁻¹ was used.

3.2.3.8 Molecular weight

Molecular weight of the PLLA/antioxidant films was determined with a gel permeation chromatograph (GPC) (Alliance GPCV 2000 system, Waters, Milford, MA, US).

PLLA/antioxidant films (20 mg) were dissolved in 10 ml of chloroform (CHCl₃) (Merck, Darmstadt, Germany), and then 50 µl of each sample solution was injected into the GPC. The GPC was equipped with an isocratic pump, an autosampler, a series of 2 columns (Waters Styragel[®] HR5E and HR4E), and a refractive index detector. A flow rate of 1 ml·min⁻¹, a runtime of 40 min, and a temperature of 35 °C were used. The Mark-Houwink corrected constant $K = 0.0131$ (mL·g⁻¹) and $a = 0.759$ for dilute PLLA solution in chloroform at 30°C was used[18].

3.2.3.9 Statistical Analysis

Statistical analyses of the PLLA/antioxidant film data were determined with SPSS software (SPSS, Inc., Chicago, IL). One-way analysis of variance using the General Linear Model procedure and Tukey's honestly significant difference (HSD) tests were used to determine significant differences ($\alpha < 0.05$).

3.3 Results and Discussion

3.3.1 Optical properties

Table 3.2 summarizes the effect of α -TOC and resveratrol on ΔE^* . It was found that the addition of antioxidants affected the $L^*a^*b^*$ values. There was a significant difference between neat PLLA and PLLA films with antioxidants. This can be attributed to α -TOC having a clear yellowish brown color and resveratrol having a dark brown color indicated by the higher a^* (redness) and b^* (yellowness) values. Statistically significant differences were found between samples with antioxidants, but these differences were not perceptible to the human eye.

Table 3.2 L^* , a^* , b^* and ΔE^* of neat PLLA and PLLA films added with α -TOC and resveratrol

Sample	L^*	a^*	b^*	ΔE^*
neat PLLA	96.22 ^a	0.24 ^a	0.21 ^a	-
T1R4	86.42 ± 0.45 ^b	7.19 ± 0.42 ^b	15.81 ± 0.64 ^b	19.70 ± 0.88 ^a
T2R3	87.65 ± 0.18 ^c	6.78 ± 0.24 ^{bc}	13.99 ± 0.50 ^{cd}	17.50 ± 0.49 ^b
T2R2	88.71 ± 0.39 ^d	5.81 ± 0.12 ^d	12.83 ± 0.36 ^c	15.71 ± 0.51 ^c
T3R2	87.98 ± 0.17 ^{cd}	6.64 ± 0.22 ^{bc}	14.10 ± 0.33 ^{de}	17.38 ± 0.40 ^b
T4R1	87.72 ± 0.13 ^c	6.57 ± 0.05 ^b	15.19 ± 0.44 ^{be}	18.35 ± 0.43 ^{ab}

Values in the same column with different superscript letters are significantly different at $\alpha = 0.05$; All of the values are expressed as average values ± standard deviation, the number of samples, n = 5:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

$$\Delta L^* = L^*_{sample} - L^*_{standard}$$

$$\Delta a^* = a^*_{sample} - a^*_{standard}$$

$$\Delta b^* = b^*_{sample} - b^*_{standard}$$

The standard value is the initial value for neat PLLA film

Figure 3.2 shows that neat PLLA films transmit almost 100% of light in the range of 800 ~ 250 nm while PLLA/antioxidant films showed a decrease in % T in the visual region, and it was dramatically reduced at 360 nm. The absorption peak found at 220 nm can be attributed to the aromatic group of resveratrol[19]. The transmission rate depended on the concentrations of the two antioxidants. The main reduction of %T from 800 ~ 460 nm might be due to the presence of α -TOC. It was also found that the %T of T1R4 showed the lowest transmission value and %T increased as the resveratrol concentration was reduced. Therefore, it can be assumed that resveratrol has a greater effect on the % T of the PLLA/ antioxidant films than α -TOC. Soto *et al.* found lower light transmission in PLA film containing resveratrol in the 350 to 200 nm region

compared to the neat PLA film[20]. Manzanarez *et al.* reported the light transmission of PLA with α -TOC decreased from 350 to 260 nm with lowest transmission at 295 nm[21],

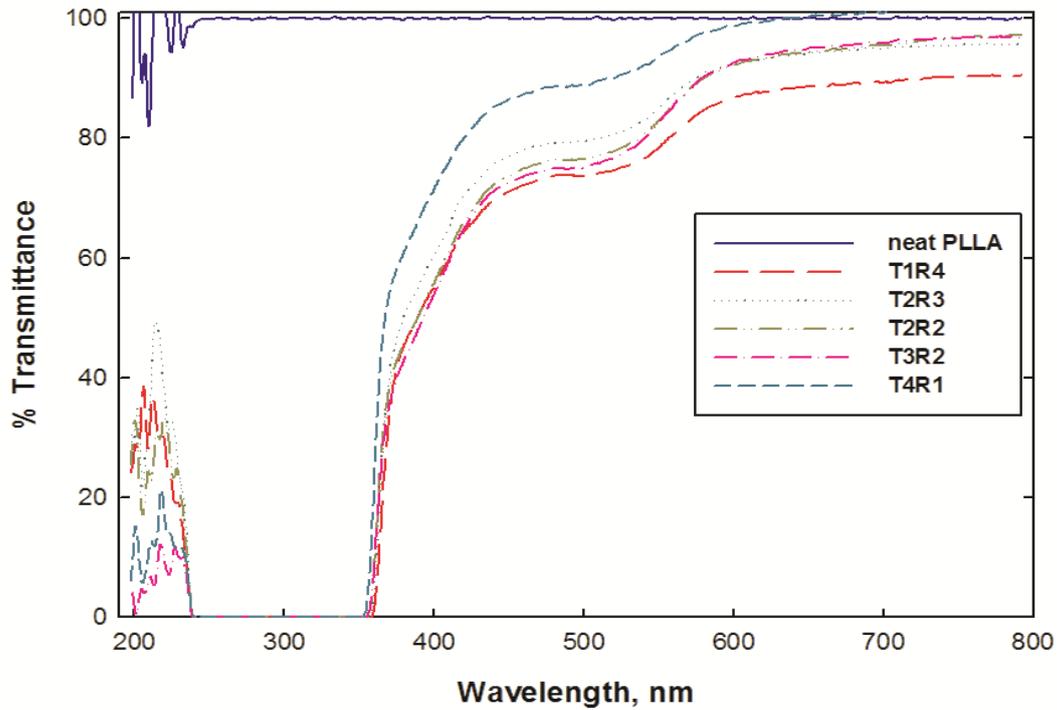


Figure 3.2 UV-VIS light transmission spectrum of PLLA/antioxidant films

In this study, the light transmission decreased from 570 nm, and this might be due to higher concentration of both antioxidants. Based on these results, PLLA films with resveratrol and α -TOC could better protect light sensitive products from UV light than PLLA films with only α -TOC.

3.3.2 Contact angle and surface tension determination

Contact angles of the samples were measured to determine any hydrophobic or hydrophilic changes in the samples. Table 3.3 lists the water and CH_2I_2 contact angles of the neat PLLA and

PLLA/antioxidant films. The water contact angle of PLLA/antioxidant films slightly increased as compared to neat PLLA films. This indicates that the addition of antioxidants made the films more hydrophobic than neat PLLA. A non-linear trend was found with the addition of α -TOC and/or resveratrol, but a clear correlation was found of increased surface tension with a large amount of antioxidants (*i.e.*, T1R4 and T3R2) due to the higher dispersive component (γ_s^d).

Table 3.3 Contact angle and surface energy of neat PLLA and PLLA/antioxidant films

Sample	Contact Angle ($^\circ$)		Surface tension ($\text{mN}\cdot\text{m}^{-1}$)		
	Water	CH_2I_2	γ_s	γ_s^d	γ_s^p
neat PLLA	78.52 ± 0.43^a	49.91 ± 1.15^a	50.99	44.29	6.70
T1R4	86.97 ± 0.93^b	41.48 ± 1.66^b	65.05	58.64	6.42
T2R3	84.08 ± 0.83^c	41.31 ± 1.71^b	57.33	50.77	6.56
T2R2	82.08 ± 0.29^d	46.16 ± 0.98^c	52.54	45.88	6.66
T3R2	85.79 ± 0.61^{bc}	45.02 ± 0.18^c	63.89	57.44	6.45
T4R1	84.41 ± 0.18^{ce}	45.81 ± 0.83^c	52.66	46.00	6.66

Values in the same column with different superscript letters are significantly different at $\alpha = 0.05$; All of the values are expressed as average values \pm standard deviation, the number of samples, $n = 5$:

3.3.3 AFM measurements

Figures 3.3 show the AFM topographical images of the PLLA/antioxidant films. The scan size of all the sample images was $10 \times 10 \mu\text{m}^2$ with a maximum of 200 nm height. The surface of the neat PLLA sample was relatively rough with an RMS roughness of 18.90 nm while the RMS values of PLLA/ antioxidant films were around 10.00 to 12.50 nm.

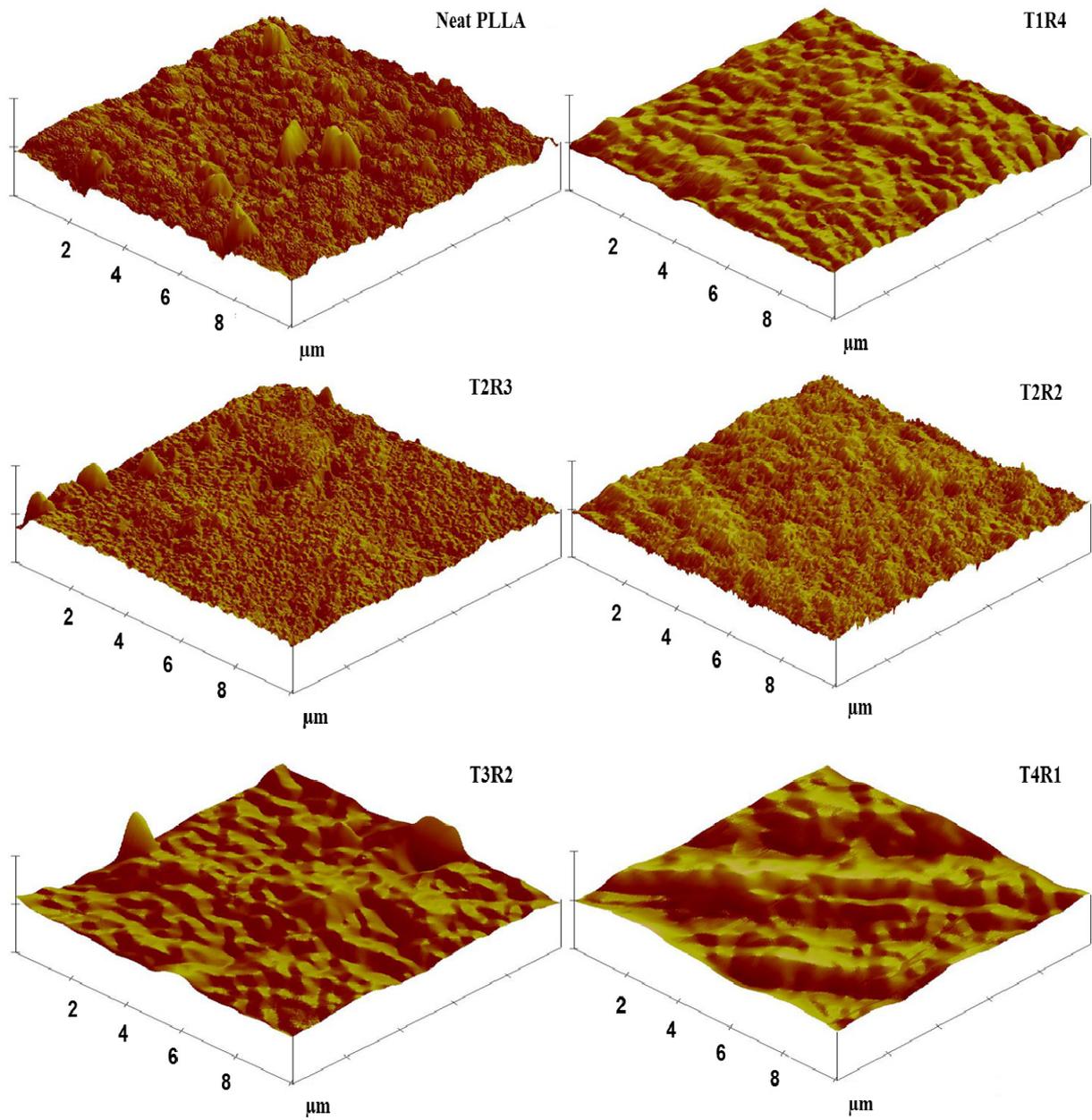


Figure 3.3 The AFM surface images of PLLA/antioxidant films; The RMS roughness of the films are 18.90 nm, 8.05 nm, 10.16 nm, 12.48 nm, 12.49 nm, and 10.00 nm, for neat PLLA, T1R4, T2R3, T2R2, T3R2, and T4R1, respectively.

This result is consistent with the increased total surface free energy. There are many factors affecting the polymer surface, especially as characterized by contact angle, such as contamination, plasticization, grafting, chemical changes, and numerous physical changes[22].

Therefore, it can be inferred that the surface tension would not have a unique role in the determination of the surface property. A glossy effect on the surface was also found on the T3R2 and T4R1 samples. The surface tensions of α -TOC and resveratrol are about 34 ~ 35 and 70 mN/m, respectively[23, 24]. It was reported that PLLA has a theoretical and experimental surface tension of 42 and 45 mN/m, respectively[25]. Therefore, it can be expected that the α -TOC with lower surface tension and at higher concentration would have a chance to migrate to the surface of PLLA/antioxidant films, and it would make the films glossier than the other PLLA films.

3.3.4 Thermal properties

The results of the thermal analysis for neat PLLA and PLLA/antioxidant films are presented in Figure 3.4 and Table 3.4. It was found that neat PLLA films showed significantly different T_g and T_m values as compared to PLLA/antioxidant films. The decrease of T_g could be attributed to the plasticizing effect of the antioxidants on the amorphous region of PLLA. Soto *et al.* recently reported similar effect of 1 ~ 3% of resveratrol on decreasing T_m and crystallinity of PLA films (about 1 °C) due to the plastization effect[20]. Manzanarez *et al.* also found a reduced T_g and T_m with addition of α -TOC in PLA film (about 1 °C)[21]. In this study, T_g and T_m were reduced about 3 ~ 5 °C; this could be due to the higher concentration of both antioxidants resulting in much greater plasticization. As seen in Figure 4, the T_{cc} peak of PLLA/antioxidant films almost disappeared indicating that the crystal growth of the PLLA chain was hindered with addition of antioxidants.

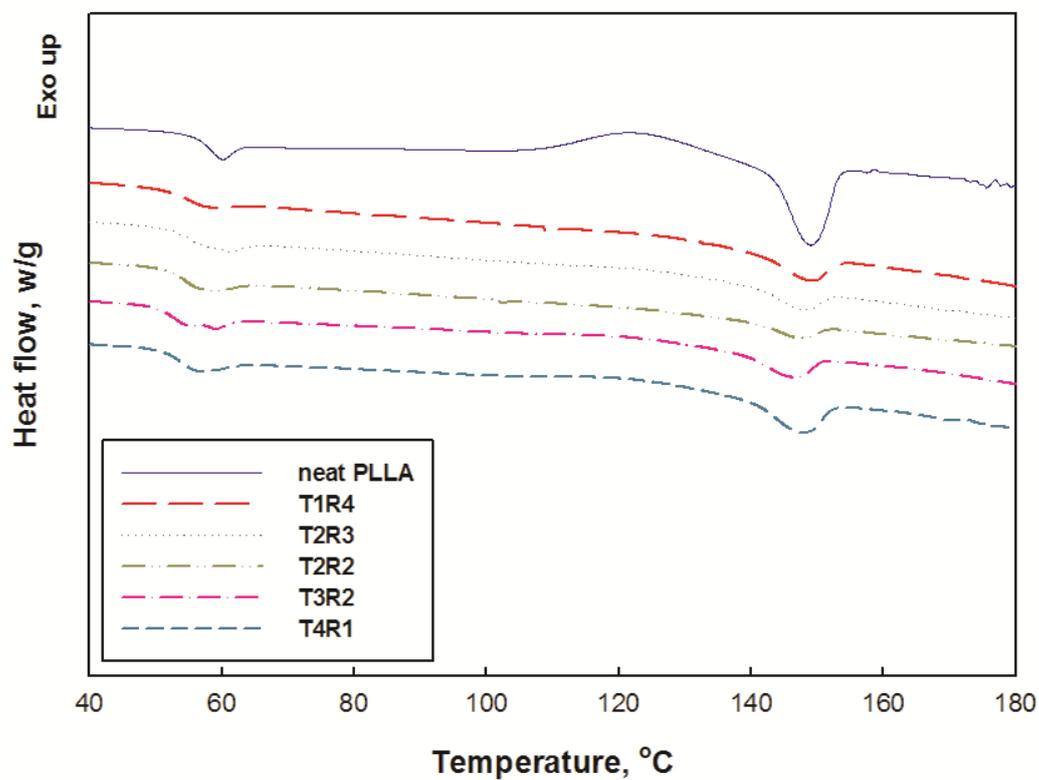


Figure 3.4 DSC thermogram of PLLA and PLLA/antioxidants films

This is confirmed by the decreased X_c of the PLLA/antioxidant samples. Statistically significant differences were found among the X_c of the PLLA/antioxidant films, indicating that the ratio of two antioxidants played a critical role in the final X_c of the films. Further studies are needed to better understand the combination effect of α -TOC and resveratrol on the X_c .

Table 3.4 Thermal properties and % crystallinity of α -TOC and resveratrol added films

Sample	T_g , °C	T_m , °C	X_c , %
neat PLLA	55.96 ± 0.45 ^a	149.01 ± 0.57 ^a	14.04 ± 1.40 ^a
T1R4	52.47 ± 0.66 ^b	143.66 ± 0.16 ^b	7.49 ± 1.45 ^b
T2R3	51.81 ± 0.73 ^{bc}	144.75 ± 0.54 ^c	5.37 ± 0.45 ^c
T2R2	52.23 ± 0.24 ^b	146.22 ± 0.60 ^d	1.71 ± 0.09 ^d
T3R2	51.05 ± 0.06 ^c	145.75 ± 0.31 ^d	1.84 ± 0.26 ^d
T4R1	50.13 ± 0.22 ^d	146.46 ± 0.45 ^d	5.16 ± 0.77 ^e

Values in the same column with different superscript letters were significantly different at $\alpha = 0.05$; All of the values are expressed as average values and standard deviation, the number of samples, n = 5:

The thermal stability of the films with antioxidants increased as compared to neat PLLA films (Figure 3.5). Arora *et al.* reported that α -TOC is thermally stable up to a temperature of about 240 °C; thereafter, it undergoes a sharp mass loss, losing about 95% of its original mass at around 460 °C[26]. In addition, resveratrol is known to have relatively good thermal stability with a melting temperature of 265 ~ 267 °C[19]. As a result, it could be concluded that α -TOC and resveratrol might act as a thermal stabilizer for the PLLA/antioxidant films, providing additional benefit for industrial production of the films (See Figure 3.5).

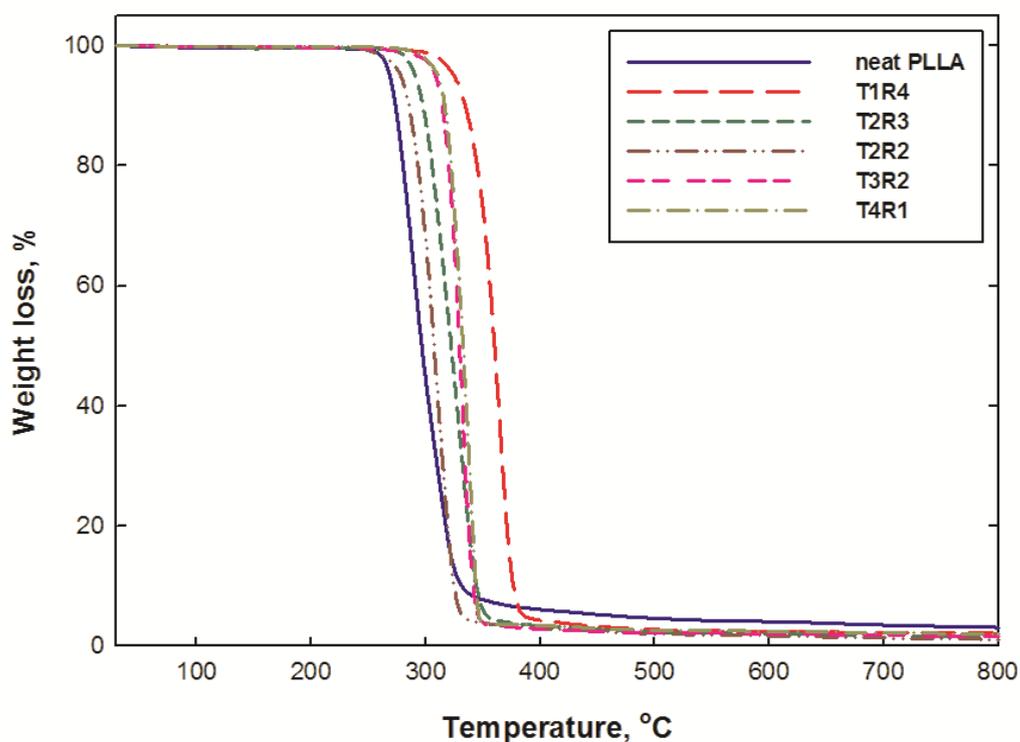


Figure 3.5 TGA analysis of PLLA/antioxidant films

3.3.5 Thermo mechanical property

Figure 3.6 (a) shows the storage modulus (G') for neat PLLA and PLLA/antioxidant films. The addition of the antioxidants increased G' . This indicates that both antioxidants could act as fillers, enhancing the elastic modulus of PLLA. Especially, resveratrol, a powder type compound, would have a greater effect on increasing the modulus (G') than α -TOC. The glassy-rubbery transition region decreased as α -TOC content increased, and this can be attributed to the plasticizing effect of α -TOC. The increased elastic modulus was found in the samples with a higher concentration of resveratrol while the plasticizing effect was observed in the samples with higher concentration of α -TOC. Therefore, the thermo-mechanical properties were highly dependent on the composition of the two antioxidants in the PLLA matrix. PLLA/antioxidant formulations could

possibly be tailored for specific applications. The increase of G' around 120°C could be due to recrystallization of PLLA crystals during the heating process[27, 28].

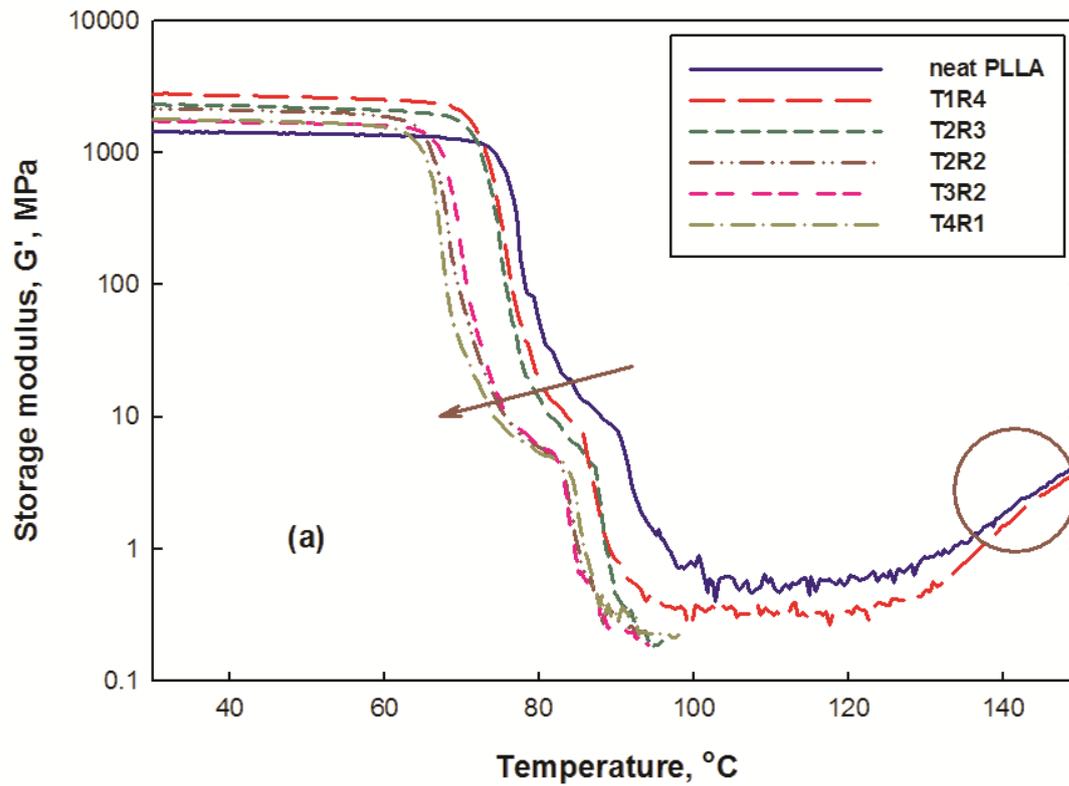
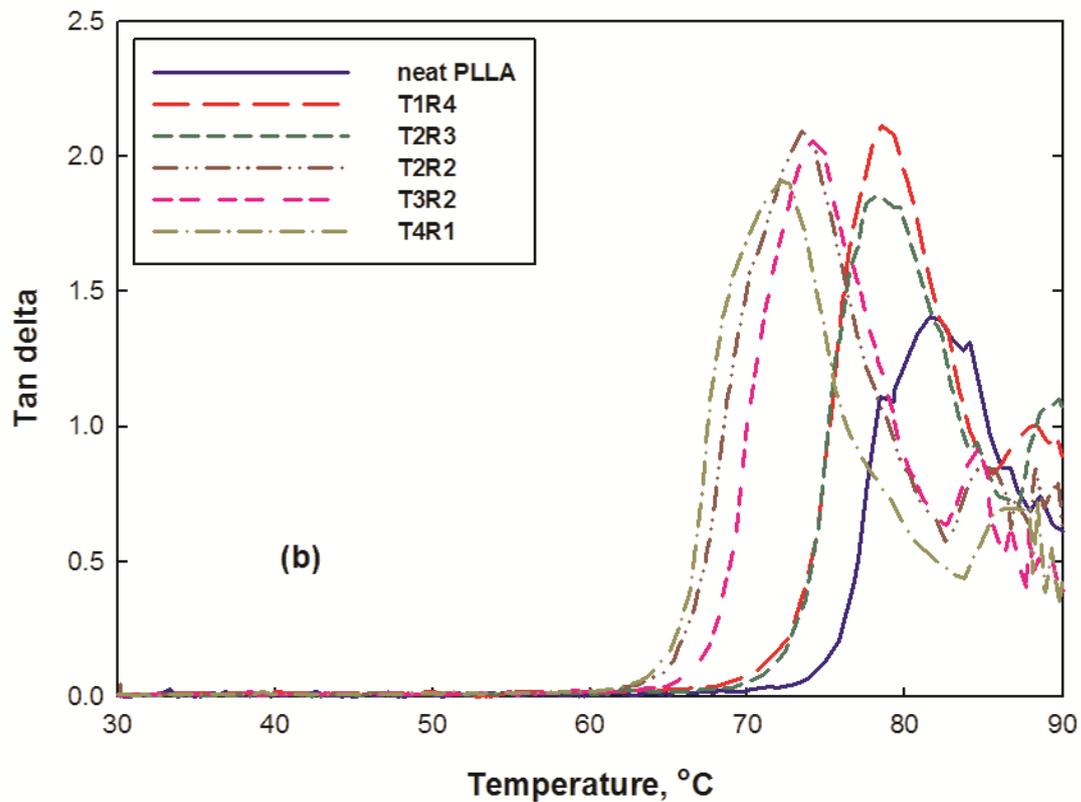


Figure 3.6 G' (a) and $\tan \delta$ (b) curve of PLLA/antioxidant films

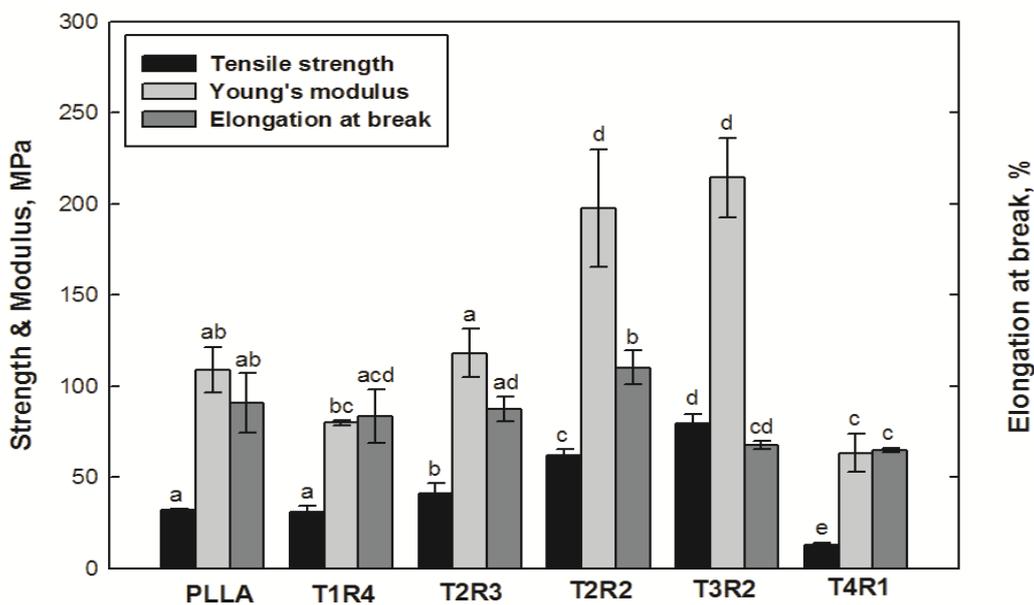
Figure 3.6 (cont'd)



As shown in Figure 3.6 (b), the $\tan \delta$ of PLLA/antioxidant films also increased as compared to neat PLLA films. This indicates that the damping property of PLLA improved due to the addition of antioxidants. The T_g , which normally coincides with the maximum $\tan \delta$, decreased for the PLLA/antioxidant films. A considerable decrease was found at higher concentration of α -TOC due to the plasticizing effect, matching the DSC results (Table 3.4).

3.3.6 Mechanical properties

Figure 3.7 shows the effect of both antioxidants on the tensile strength and Young's modulus of the neat PLLA and PLLA/antioxidant films. The tensile strength and modulus were expected to decrease with lower X_c . However, an increase of tensile strength was found for samples with antioxidants except for the T4R1 sample. It appears that resveratrol restricts the mobility of the amorphous region and stiffens the PLLA films. In this study, T2R2 and T3R2, which had the lowest X_c , had the highest tensile strength and modulus. In the case of the T4R1 samples, a reasonable assumption is that an amount of α -TOC beyond some critical point weakens the intermolecular forces between adjacent PLLA chains and causes disentanglement, giving the final material poor mechanical properties.



Note: Values with the same color bar and with different letters are significantly different at $\alpha = 0.05$; All of the values are expressed as average values \pm standard deviation, number of samples, $n = 5$.

Figure 3.7 Tensile strength, Young's modulus, and Elongation at break of PLLA/antioxidant films.

3.3.7 Rheological properties

Figure 8 shows the rheological properties, dynamic complex viscosity and modulus of neat PLLA and PLLA/antioxidant films at 190°C. Neat PLLA films showed almost Newtonian behavior in the $1 \sim 10 \text{ rad}\cdot\text{s}^{-1}$ frequency range, and exhibited non-Newtonian behavior in the high frequency region ($100 \text{ rad}\cdot\text{s}^{-1}$). The other samples behaved similarly, and no shear thinning was observed in the samples. The melt viscosity of the PLLA/antioxidant films was substantially higher than that of neat PLLA films. In the case of T2R3, the melt viscosity was much higher than that of the other PLLA/antioxidant films, and this increase could be related to the formation of chain entanglements between PLLA and both antioxidants. Ray *et al.* reported that the master curves of PLLA melt in the terminal region (low frequency region) can be represented by the power law of $G'(\omega) \propto \omega^2$ and $G''(\omega) \propto \omega$, similar to those of narrow M_w distribution homopolymer melts[27]. The slopes of the terminal regions of neat PLLA and PLLA/antioxidant films were determined (Table 3.5). The correlation coefficients (r^2) were found to be 0.999. The slopes of $G'(\omega)$ and $G''(\omega)$ for neat PLLA in the terminal region were found to be 0.169 and 0.936, respectively. These values are in a good agreement with the results reported by Ray *et al.*[29] and Gu *et al.*[30]. The slopes of $G'(\omega)$ and $G''(\omega)$ for PLLA/antioxidant melts did not differ much from those of neat PLLA films. The $G'(\omega)$ of the PLLA/antioxidant films show higher values compared with that of neat PLLA over the entire frequency range, and this higher $G'(\omega)$ could be an indication of formation of entanglement between PLLA and both antioxidants, which is consistent with the DMA results (Figure 3.6).

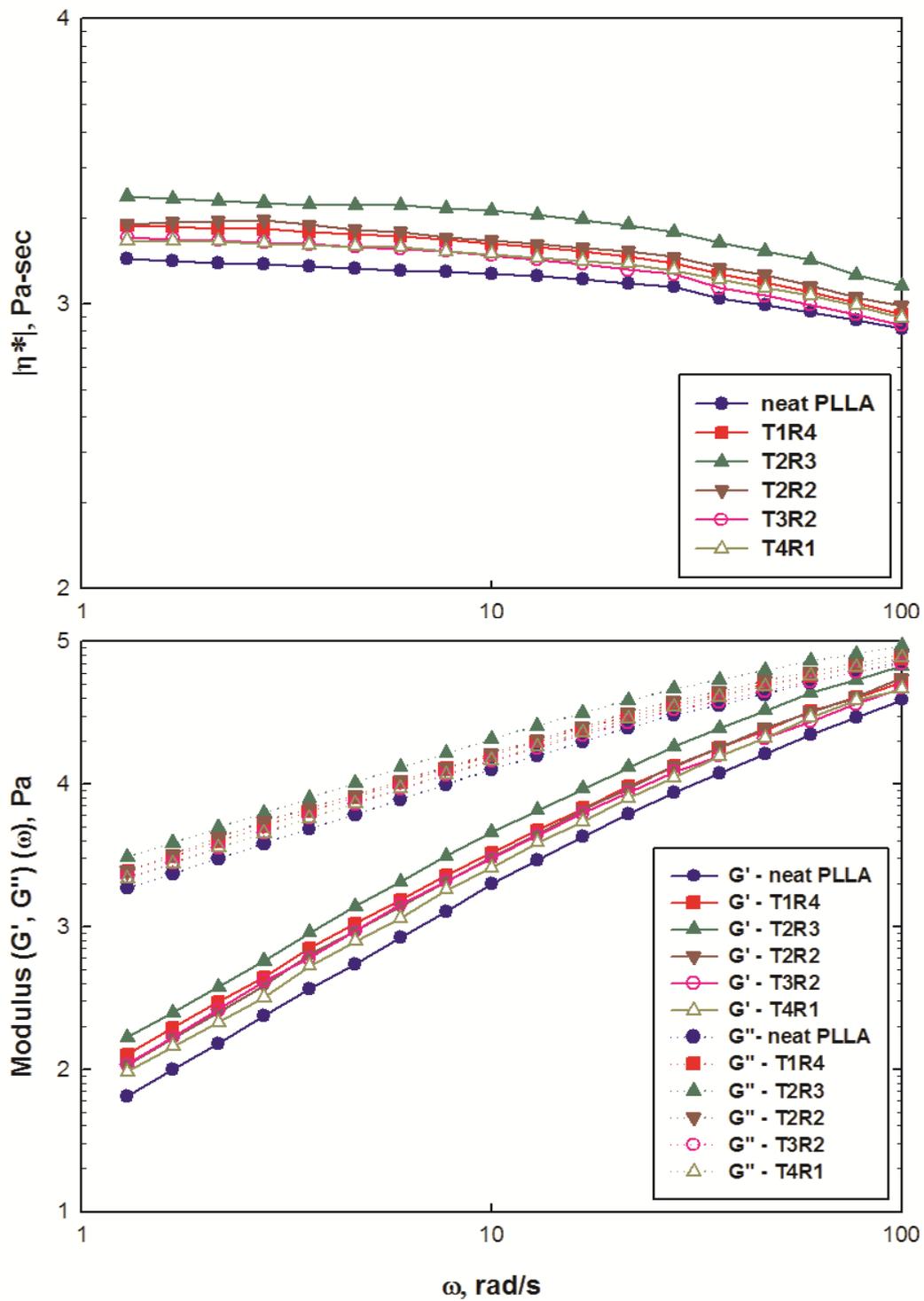


Figure 3.8 Complex viscosity (η^*), storage modulus (G'), and loss modulus (G'') of the PLLA/antioxidant films as a function of frequency at 190°C.

Table 3.5 The melt rheological characteristic of neat PLA and PLA/antioxidants melts

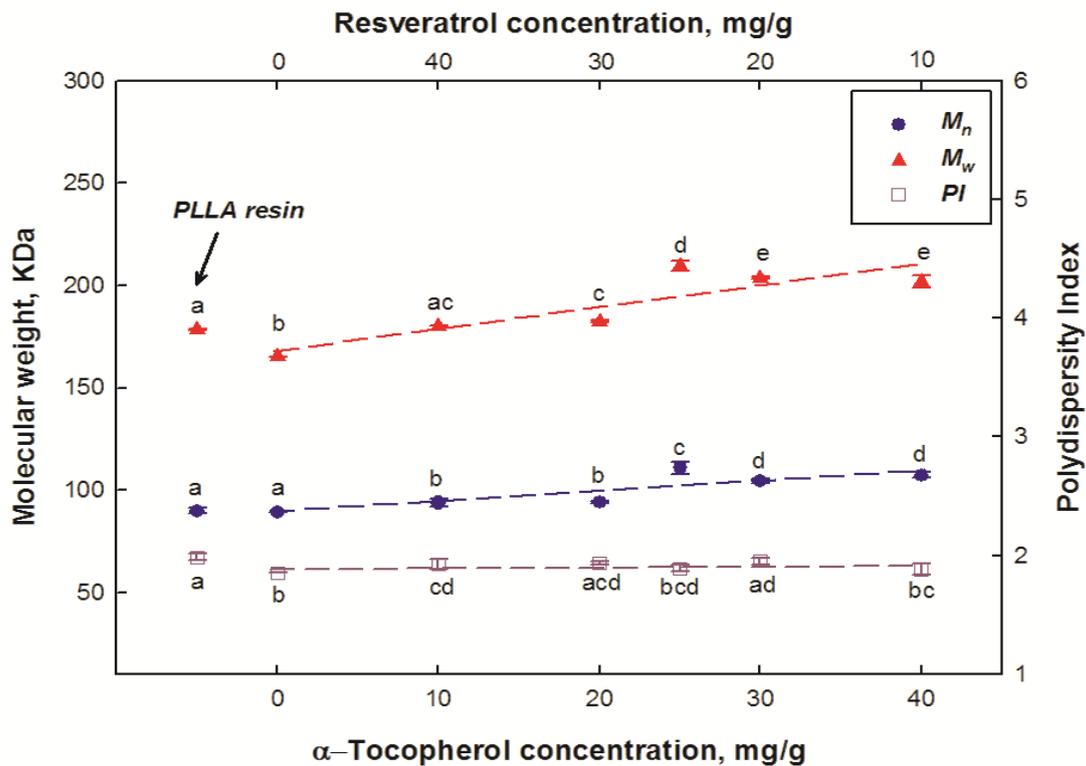
Sample	neat PLLA	T1R4	T2R3	T2R2	T3R2	T4R1
Terminal region slope of $G'(\omega)$	1.669 ± 0.008^a	1.62 ± 0.014^b	1.648 ± 0.009^{ab}	1.668 ± 0.018^a	1.658 ± 0.017^{ab}	1.646 ± 0.018^{ab}
Terminal region slope of $G''(\omega)$	0.936 ± 0.002^a	0.929 ± 0.006^a	0.941 ± 0.004^a	0.929 ± 0.002^a	0.931 ± 0.003^a	0.948 ± 0.006^a

Values in the same row with different superscript letters were significantly different at $\alpha = 0.05$; All of the values are expressed as average values and standard deviation, the number of samples, $n = 5$:

3.3.8 Molecular weight

Figure 3.9 shows a gradual increase in number and weight average molecular weight (M_n and M_w) of the samples with added antioxidants, while the polydispersity index (PI) remained stable.

This slight increase of M_w can be attributed to an increase of chain entanglements between PLA and antioxidant chains in the amorphous regions. It could also be possible to have physical crosslinks by intermolecular forces between PLLA chains and adjacent antioxidant chains. The M_w increase could account for the increase in mechanical properties (except T4R1) illustrated in Figure 7. This result could be partly correlated and explained by the high thermal stability of PLLA/antioxidants films.



Note: Symbols with the same color and with different letters are significantly different at $\alpha = 0.05$; All of the values are expressed as average values \pm standard deviation, the number of samples, $n = 5$.

Figure 3.9 Number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PI) of PLLA/antioxidant films.

3.4 Conclusions

Poly(94% L-lactic acid) resin was melt compounded with α -TOC and resveratrol to produce PLLA/antioxidant films. The addition of α -TOC and resveratrol increased the a^* (redness) and b^* (yellowness) values of the PLLA/antioxidant films. These samples showed slightly more hydrophobic characteristics than neat PLLA films due to the energy dispersive component. Increase in the elastic modulus with varying concentrations of the two antioxidants was found in PLLA/antioxidant films. The combinations of α -TOC and resveratrol have a critical role on %T,

T_g and X_c . Both antioxidants affected the mechanical and thermo-mechanical properties of PLLA films. The melt viscosity of the PLLA/antioxidant films was substantially higher than that of neat PLLA. The $G'(\omega)$ of the PLLA/antioxidant films was found to be higher than that of neat PLLA films over the entire frequency range. These higher melt viscosity and $G'(\omega)$ values could be an indication of formation of entanglements between PLLA and α -TOC and resveratrol. These results show potential feasibility for using PLLA/antioxidant films as active functional membranes for food, pharmaceutical, and medical packaging applications.

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CHAPTER IV

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CHAPTER IV

Grafting of Maleic Anhydride on Poly(L-lactic acid). Effects on Physical and Mechanical Properties

Abstract

Maleic Anhydride (MAH) was grafted on poly(L-lactic acid) (PLLA) in the presence of dicumyl peroxide (DCP) as a radical initiator. The effect of the MAH and DCP concentrations on the grafting and the physical and mechanical properties of PLLA films were investigated. The glass transition temperature and crystallinity significantly decreased on addition of MAH. The thermal decomposition of the PLLA films was affected by the MAH content while the mechanical properties were almost unchanged. A slight increase in molecular weight was found, which could be attributed to either the MAH branching reaction or a possible crosslinking reaction between the PLLA chains increasing the chain entanglements.

4.1 Introduction

Poly(lactic acid) (PLA) a biodegradable, compostable, and recyclable thermoplastic has attracted a lot of commercial attention because it can be produced from renewable resources. PLA has good mechanical properties comparable to polystyrene (PS) and poly(ethylene terephthalate) (PET). Commercial PLA is generally obtained from ring-opening polymerization of lactide as a monomer. Lactide is the cyclic dimer prepared by the controlled depolymerization of lactic acid, acquired by the fermentation of corn, sugar cane, and sugar beets[1, 2]. PLA is currently being used in disposable packaging applications formed by techniques such as thermoforming, injection molding, and extrusion.

Although PLA consumption and sales volume have increased in the last decade, its stiff and brittle properties and processing instability (*i.e.*, low melt viscosity limiting its processing through blow molding or foaming) have been major drawbacks for extended commercialization. Furthermore, the absorption of moisture during processing induces hydrolysis in PLA and impacts its melt properties. The melt viscosity of a polymer usually depends on several molecular characteristics, such as the weight-average molecular weight (M_w), the molecular weight distribution (MWD), and the degree of branching or crosslinking. PLA branching and crosslinking can be controlled by the addition of melt processing additives and/or grafting. Chemical modification using free radical reactions has been evaluated extensively in polypropylene (PP) and polyethylene (PE) for controlled degradation or branching, and in aliphatic polyesters like PLA and Poly(butylene adipate-co-succinate)(PBAS) for decreasing branching or crosslinking[3-6]. Other common routes to improve PLA properties are the use of plasticizers, copolymerization, and/or blending. Blending of PLA with other polymers (non-biodegradable or biodegradable polymers) is a useful technique not only to impart flexibility and

toughness to the PLA, but also to reduce material cost. Various polyolefins and vinyl polymers have been used for PLA blending to improve its properties[7-10]. PLA has also been blended with biodegradable polymers such as aliphatic polyesters and aliphatic–aromatic copolyesters[11-13].

Polymers with functional groups such as -OH, -COOH or -NH₂ in their chain ends can be chemically coupled with reactive polymers such as maleic anhydride[11, 12], oxazoline[13, 14], and epoxide[15-17]. Compatibilizers formed by chemical reactions between polymer chains that are mutually reactive are called “*in-situ formed compatibilizers.*” During the compatibilization process, small dispersed phases (or domains) are formed, enhancing the interfacial adhesion and reducing the interfacial tension between two immiscible polymers[18, 19].

Maleic anhydride (MAH) is one of the most widely used reactive compatibilizers due to its good chemical reactivity, low toxicity, and low potential to polymerize itself under free radical grafting conditions[20]. Gaylord *et al.* reported the formation of single and oligomeric grafts by grafting of MAH onto polyolefins, and proposed that a bridge could be formed between grafted MAH and polymer chains[21-23]. Zhang *et al.* investigated the effect of MAH with a radical initiator, 2,5-bis(tert-butylperoxy)-2,5 dimethylhexane (Luperox[®] 101) for PLA/wheat starch blends prepared by a reactive compatibilization method. The interfacial adhesion effectively improved, and the highest tensile strength and elongation at break were found in the blends of 55 % PLA and 45% starch composition ratio with 1% MAH[24]. The addition of 3 and 5 phr PLA-g-MA to the PLA/wheat straw composites resulted in significant improvements of the tensile strength (20%) and flexural strength (14%)[25]. However, these improvements are not sufficient to meet the industrial requirements of PLA resin.

In this study, the impact of dicumyl peroxide (DCP) as initiator in the grafting of MAH onto PLLA to form PLLA-g-MAH was evaluated, and then thermal and mechanical properties of PLLA-g-MAH produced with different amount of DCP was investigated. In addition, the molecular weight change was monitored to determine the optimized concentration of DCP and MAH as a feasible compatibilizer for future PLA blends.

4.2 Experimental

4.2.1 Materials

PLA resin, 4042D grade (94% L-lactic acid) (PLLA) (NatureWorks LLC, MN), was used and dried in a vacuum oven at 60 °C for 24 h to remove residual moisture. DCP and MAH (briquettes, 99%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). All chemicals were used as received.

4.2.2 Preparation of maleated PLLA (PLLA-g-MAH)

The PLLA-g-MAH was prepared in an intermixer, Brabender Plasticoder, PLE 331 (Brabender, Duisburg, Germany) at 190°C with a rotor speed of 60 rpm. The PLLA was melted for 2 min, and then DCP (0.1 ~ 0.2 phr) as a free radical initiator was added and mixed for 3 min. The modification reaction with the MAH (0.5 ~ 3.0 phr) continued by mixing another 5 min. The formulations used for producing PLLA-g-MAH are listed in Table 4.1. The PLLA-g-MAH, yellow color strips, was taken out and ground into small pieces with a grinder, DHG14 (Daeheung Tech, Daegu, Korea).

Table 4.1 Formulations used to produce PLLA-g-MAH samples

DCP (phr)	Maleic anhydride (phr)				
	0	0.5	1	2	3
0.1	D1M00	D1M05	D1M10	D1M20	D1M30
0.2	D2M00	D2M05	D2M10	D2M20	D2M30

The PLLA-g-MAH sample films with thickness of 150 ~ 200 m were prepared by compression molding process in a hydraulic laboratory press model 3925 (Carver, Wabash, IN) with a pressure of 150 Kg_f·cm⁻² for 3 min at 200 °C. The chemical reaction between PLLA and MAH previously described by Zhang *et al.*[24] is shown in Figure 4.1.

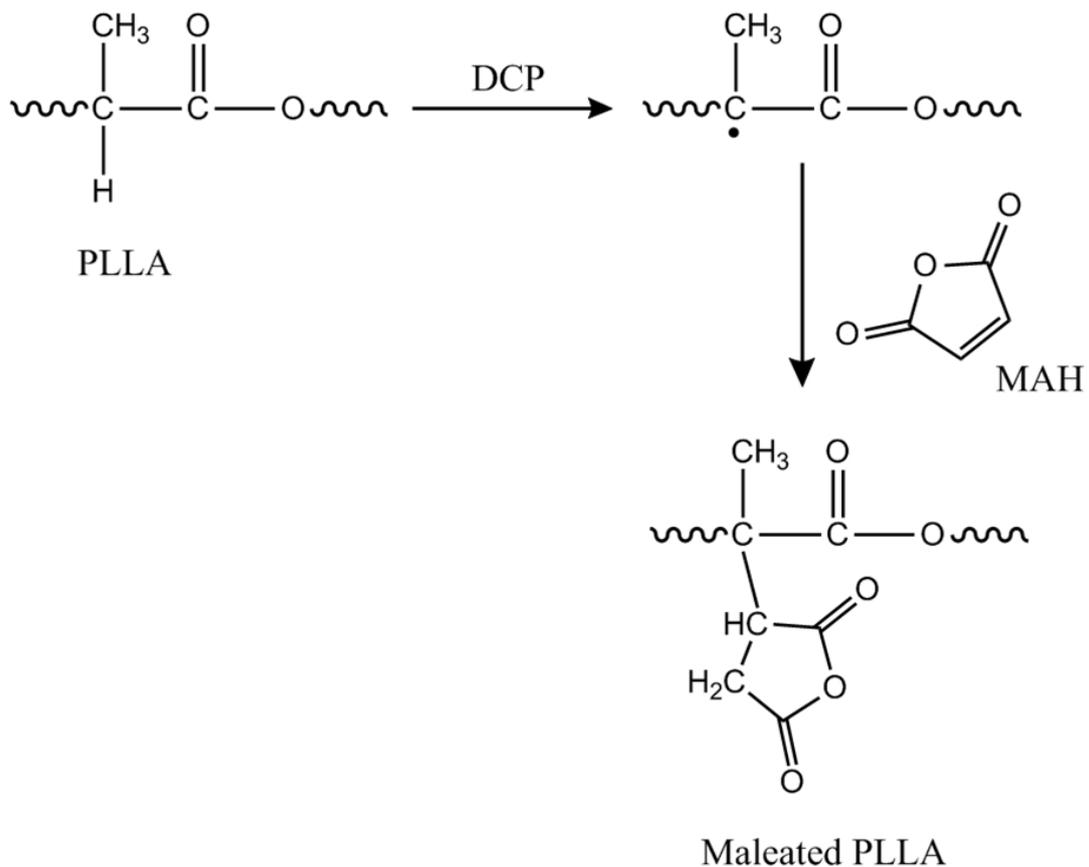


Figure 4.1 Proposed chemical reaction of PLLA and MAH

4.2.3 Characterizations

4.2.3.1 Spectrophotometric analysis

In order to evaluate how much MAH was grafted, Fourier transform infrared (FT-IR) spectroscopic analysis was carried out on the neat PLLA and PLLA-g-MAH films with a Varian FT-IR spectrometer (660-IR, Palo Alto, CA, USA). A total of 40 scans in % transmission mode were performed over the 4000 ~ 650 wavenumber range. Five samples were tested for each specimen and composition.

For $^1\text{H-NMR}$ analysis, the PLLA-g-MAH film samples were dissolved in CDCl_3 and sealed in NMR tubes. Analysis was performed with a $^1\text{H-NMR}$ spectrometer (Bruker AVANCE III 500, Billerica, MA, USA) with a 5mm BB probe at 500.15 MHz operating frequency, and a spectral window of -2 to 10 ppm.

4.2.3.2 Gel content and grafting yield

The gel content of the samples was determined according to a modified ASTM D2765 method where a soluble fraction of the samples were extracted with refluxing chloroform. The soluble fractions of the PLLA-g-MAH films were extracted for 24 h through an ADVANTEC thimble filter (Toyo Roshi Kaisha, Ltd, Japan). The insoluble fractions of the PLLA-g-MAH films were dried in a vacuum oven at 60 °C for 24 h, and the amount of the cross-linked (gel) fraction was determined gravimetrically using equation (1).

$$Gel\ content\ (\%) = \frac{W_1 - W_3}{W_2 - W_3} \times 100 \quad (1)$$

where W_1 = the weight of specimen and thimble filter after extraction

W_2 = the weight of specimen and thimble filter before extraction

W_3 = the weight of thimble filter

The grafting yield was determined by titration analysis according to a modified procedure[26]. The sample was dried at 130 °C under a vacuum to evaporate any unreacted MAH. The grafted sample (1.15 ± 0.01 g) was then dissolved in 150 mL of chloroform, and 1.5 mL of 1 M hydrochloric acid in water was added. The solution was stirred vigorously for 45 min. The grafted polymer was selectively recovered by precipitation into methanol, followed by filtration, then drying at 80 °C for 15 h. Samples of 1.15 ± 0.01 g were completely dissolved in 100 mL of a mixed solution of chloroform: methanol (3:2 v/v), and 8~10 drops of 1% phenolphthalein in ethanol were added. The titration was carried out with 0.03 N of potassium hydroxide (KOH) in methanol, and the pH of the samples at end point was determined. The percentage of MAH grafting was calculated according to equations 3 to 5.

$$\text{Normality of KOH} = \frac{g\ KHP \times \text{purity of KHP}(\% \text{ fraction})}{L\ KOH \cdot 204.22} \quad (2)$$

$$\text{Acid number}(\text{mg KOH/g}) = \frac{mL\ KOH \cdot N\ KOH \cdot 56.1}{g\ \text{polymer}} \quad (3)$$

$$\% \text{ MAH grafting} = \frac{\text{Acid number} \times 98.06}{2 \times 561} \quad (4)$$

where KHP is the amount of potassium hydrogen phthalate.

4.2.3.3 Thermal properties

The glass transition temperature (T_g), melting temperature (T_m), and percent crystallinity (X_c) of the samples were determined with a differential scanning calorimeter (DSC) (Diamond™ DSC, Perkin-Elmer, Waltham, MA, USA). The analyses were carried out under nitrogen atmosphere and a temperature range from 20 to 220 °C at a heating rate of 5 °C·min⁻¹, and were analyzed by Diamond Analysis software. The heat of fusion (93.1 J·g⁻¹)[27] for 100 % PLA was applied to determine the percent crystallinity using the following equation (5).

$$x_c(\%) = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^c} \times 100 \quad (5)$$

where ΔH_m is enthalpy of fusion, ΔH_c is the enthalpy of cold crystallization, ΔH_m^c is enthalpy of fusion of pure crystalline PLA; $\Delta H_m^c = 93.1 \text{ J}\cdot\text{g}^{-1}$ [27].

Thermal gravimetric analysis (TGA) (Q600, TA Instruments, New Castle, DE, USA) was used to assess the thermal stability of the PLLA-g-MAH samples. The measurements were performed under nitrogen atmosphere and up to 800 °C with a heating rate of 10 °C·min⁻¹.

4.2.3.4 Thermo-mechanical and mechanical properties

Dynamic mechanical analysis (DMA) of the PLLA-g-MAH films was performed on a Triton Technology DMA (TTDMA) from Triton Technology Ltd., Keyworth, UK. Samples with a width of 6.0 – 6.5 mm and a length of 12 -15 mm were cut for testing in DMA in tension mode. All the sample dimensions were carefully measured and the mean values of 6 measurement

points of the samples were recorded. The measurement was carried out at a heating rate of $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ and a temperature range of -30 to $160\text{ }^{\circ}\text{C}$ with a frequency of 1 Hz . The storage modulus, G' was measured for each sample in this temperature range.

Tensile strength, Young's modulus, and elongation at break were assessed using a Universal Test Machine (UTM) (Instron 4465, Instron, Canton, MA) according to ASTM D 882-02. The samples were cut into strips with dimensions of $1 \times 8\text{ cm}$ and conditioned at $23\text{ }^{\circ}\text{C}$ and 50 \% RH for at least 24 h . The specimens were tested at a crosshead speed of $10\text{ mm}\cdot\text{min}^{-1}$. At least five specimens were tested for each composition.

4.2.3.5 Molecular weight

Molecular weight of PLLA-g-MAH films was determined with a gel permeation chromatograph (GPC) (Alliance GPCV 2000 system, Waters, Milford, MA, US). Twenty mg of PLLA-g-MAH films were dissolved in 10 ml of chloroform (CHCl_3 , 99.9%) (Merck, Darmstadt, Germany) and 50 L of each sample solution was injected into the GPC. The GPC was equipped with an isocratic pump, an autosampler, a series of 2 columns (Waters Styragel HR5E and HR4E), and a refractive index detector. A flow rate of $1\text{ mL}\cdot\text{min}^{-1}$, a runtime of 40 min , and a temperature of $35\text{ }^{\circ}\text{C}$ were applied. The Mark-Houwink constants $K = 0.0131\text{ (mL}\cdot\text{g}^{-1})$ and $a = 0.759$ for chloroform at $30\text{ }^{\circ}\text{C}$ for dilute PLLA solution were used[28].

4.2.3.6 Melt flow Index

The melt flow Index (MFI) of the original and modified PLLA-g-MAH films was measured by a melt flow indexer (DAVENPORT MFI-10) (Hants, UK). The PLLA was placed in the capillary

of the melt flow indexer at temperatures around 190°C, and then the melt flow changes were measured. A load and cutting time of 2.16 kg and 60 s, respectively, were used. Five samples were tested for each composition.

4.2.3.7 Statistical analysis

Statistical analyses of the PLLA and PLLA-g-MAH films data were conducted with SPSS software (SPSS, Inc., Chicago, IL). One-way analysis of variance using the General Linear Model (GLM) procedure and Tukey's honestly significant difference (HSD) tests were used to determine significant differences ($P < 0.05$).

4.3 Results and Discussion

The sample films were prepared from prepared PLLA-g-MAH which used DCP as an initiator. Films were evaluated to understand the degree of the grafting reaction of MAH on PLLA.

4.3.1 Spectrophotometric analysis

Figure 4.2 shows the FT-IR spectra of PLLA-g-MAH samples with different concentrations of DCP. The characteristic adsorption bands at 1850 cm^{-1} correspond to asymmetric stretching of the carbonyl group (C=O) of the cyclic anhydride. The peak band at 1590 cm^{-1} corresponds to the cyclic C=C stretching of anhydride. Absence of the adsorption peaks at 1590 cm^{-1} was found for D1M05, D1M10, D2M05 and D2M10 samples, suggesting that the MAH was grafted onto the PLLA. Some unreacted MAH should be expected for samples with a high concentration of MAH. This was consistent with the absence of a peak band at 695 cm^{-1} corresponding to

aromatic C-H bending. (Figure not shown) Since the added amount of MAH (0.5 – 3.0 phr based on PLLA) was small, the asymmetric stretching of the C=O (1774 cm^{-1}) could have a weak intensity, and could overlap with the C=O of the PLLA.

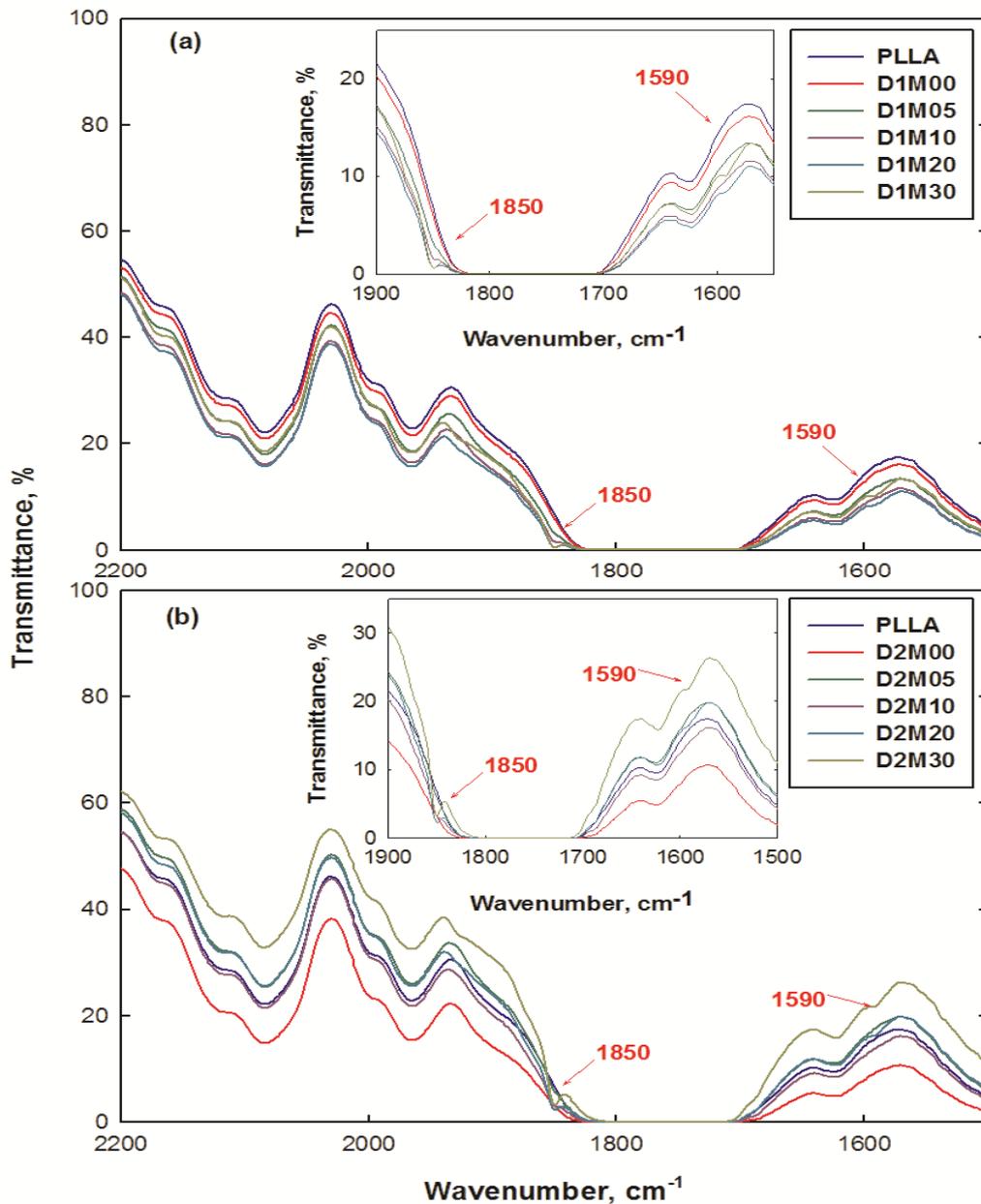


Figure 4.2 FT-IR spectra of maleated PLLA samples with different DCP contents: (a) 0.1 phr and (b) 0.2 phr

Figure 4.3 shows the $^1\text{H-NMR}$ spectra of the PLLA-g-MAH samples. The succinyl functional groups generally are found in the region of 2-3 ppm[29, 30]. A peak at 2.25 ppm was evident for the D1M10 samples but not for PLLA samples. The spectra obtained for all other PLLA-g-MAH samples showed the same peaks (Figures not shown). This result supports the conclusion from the FT-IR data that MAH was grafted onto PLLA.

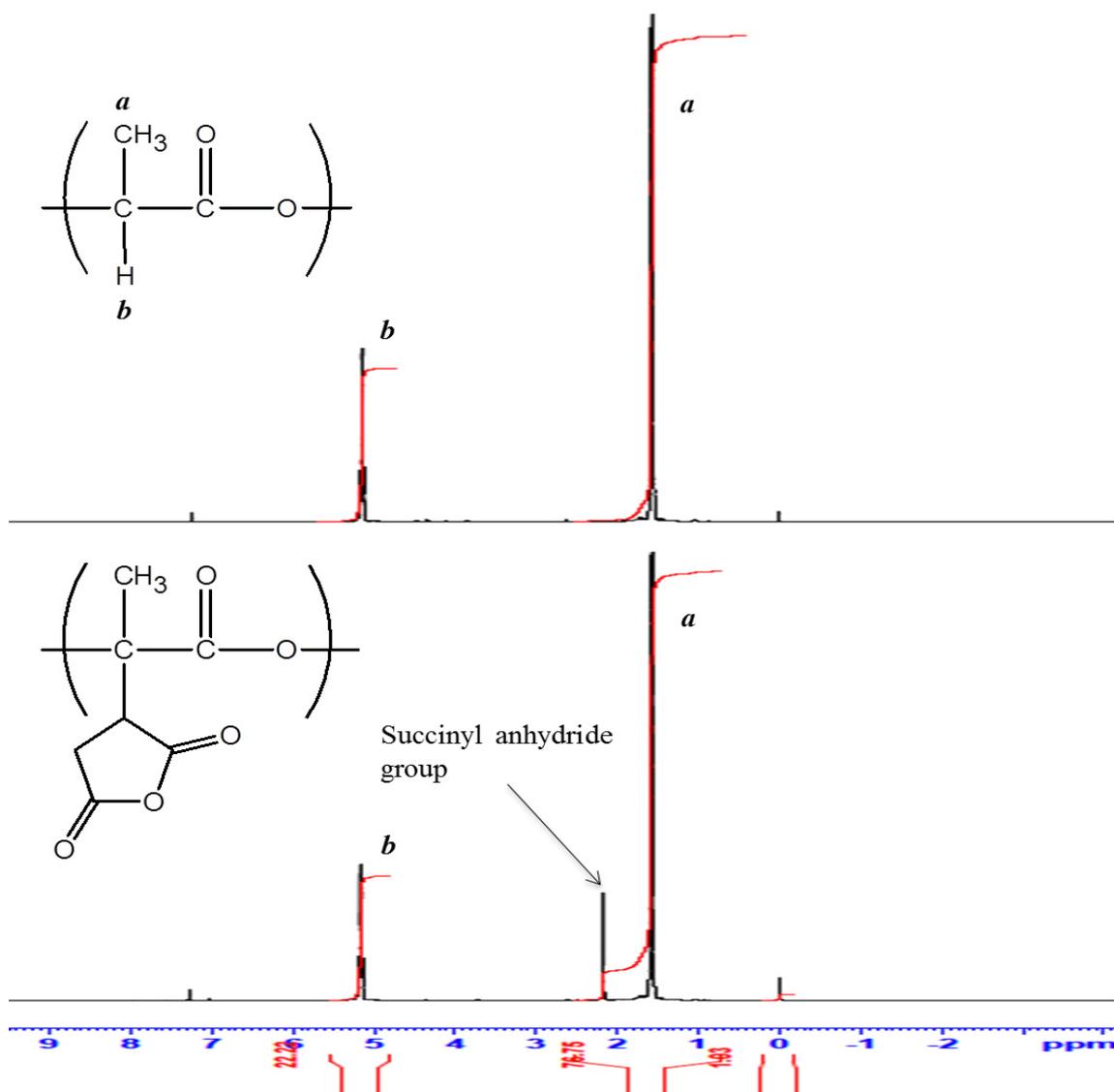
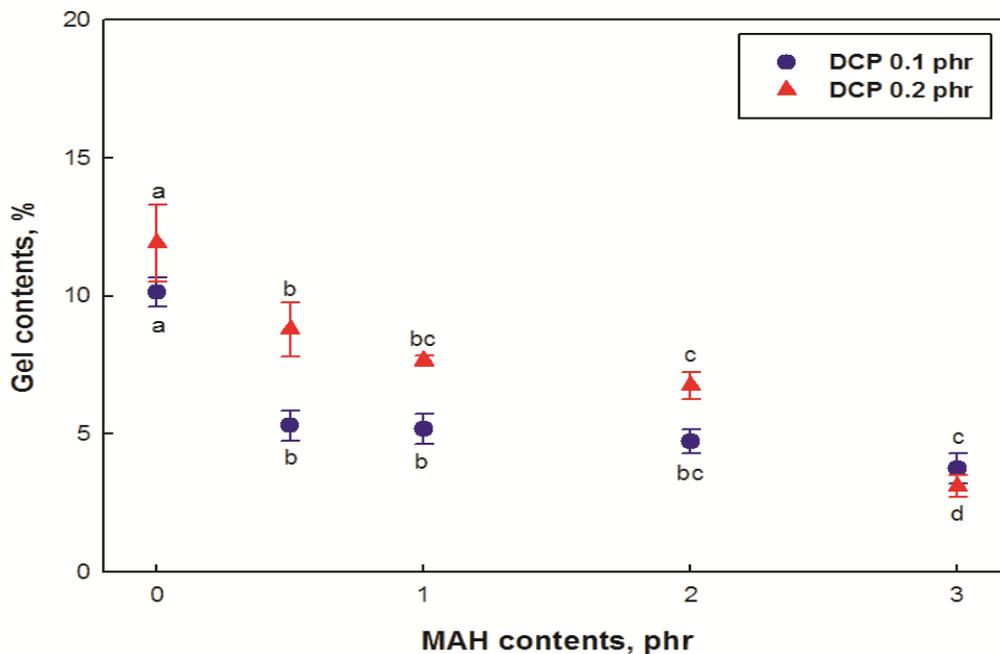


Figure 4.3 $^1\text{H-NMR}$ spectra of neat PLLA sample (top) and D1M10 sample (bottom)

4.3.2 Gel contents and grafting yield

The analysis of gel content showed that the addition of DCP caused the crosslinking of PLLA samples (Figure 4.4). Tacamura *et al.* examined the crosslinking reaction with a variety of peroxides under constant mole ratio, and confirmed that DCP has an effect on the crosslinking reaction of PLLA, especially at longer extrusion times[31]. It was also recently reported that the addition of DCP during PLLA modifications caused crosslinking of PLA as well as an increase in degree of swelling[32]. The gel content decreased with introduction of MAH onto the PLLA samples. It can be assumed that the free radicals formed in the PLLA chain in the presence of higher concentration of DCP could have been reacted with the anhydride group of MAH, reducing the active sites for crosslinking reactions among the PLLA chains, resulting in decreased gel content.



Note: Values in the same symbol with different letters are significantly different at $\alpha = 0.05$.

Figure 4.4 Gel contents of PLLA-g-MAH samples with different amounts of DCP.

Table 4.2 The MAH grafting yield with different amounts of DCP

Samples	Grafting yield, %
D1M00	n/a
D1M05	0.08
D1M10	0.12
D1M20	0.34
D1M30	0.38
D2M00	n/a
D2M05	0.13
D2M10	0.18
D2M20	0.39
D2M30	0.43

The MAH grafting yield determined by the titration method is listed in Table 4.2.

As MAH content increased at constant DCP content, the grafting yield increased. Mani *et al.* investigated the effect of peroxide initiator and MAH contents on the grafting yield, and reported that the higher initiator concentration affects the total free radical concentration while the MAH concentration may only have effect on improving the grafting yield. In addition, an initiator concentration more than 1 wt.-% can cause greater crosslinking, resulting in decreased grafting yield[33]. In the current study, relatively low DCP contents (0.1 ~ 0.2 phr) were used; therefore, a higher grafting yield (> 0.5%) could be expected if DCP concentration is increased.

4.3.3 Thermal properties

The DSC thermogram given in Figure 4.5 shows that the T_g of PLLA-g-MAH made with 0.1 phr of DCP decreased as MAH content increased. The endothermic peaks at T_g could be attributed to

the enthalpy relaxation effects coming from the thermal history of the samples[34]. Samples with 0.2 phr of DCP also show the same behavior (Figure not shown).

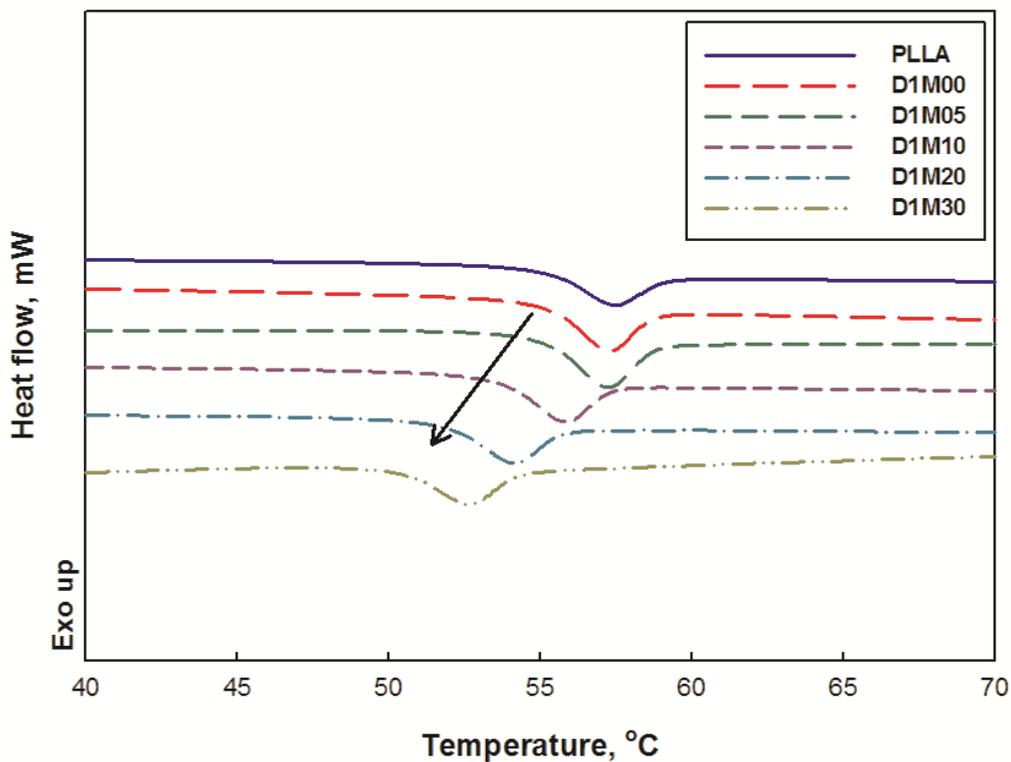


Figure 4.5 The DSC thermograms of neat PLLA and maleated PLLA samples with 0.1 phr of DCP

Table 4.3 summarizes the thermal characteristics, T_g , T_m , and X_c of neat and maleated PLLA samples acquired from the first heating scan. The T_g and % X_c were significantly decreased by the addition of MAH while T_m was slightly reduced. The reduction of T_g could be attributed to chain branching due to a grafting reaction between PLLA and MAH resulting in an increase of segmental mobility of PLLA chains. In addition, this irregular chain branching of MAH onto the PLLA backbone might decrease regularity and hinder the crystalline growth of PLLA, resulting

in lower crystallinity. The crystallization temperature reduced slightly with addition of DCP due to the crosslinking, and tends to decrease as MAH content increases. This could be attributed to the branching reaction of MAH onto the PLLA chains.

Table 4.3 Thermal properties and % X_c of PLLA-g-MAH films obtained from the first heating scan

Samples	T_g , °C	T_m , °C	T_c , °C	X_c , %
neat PLLA	54.9 ± 0.1 ^a	165.8 ± 0.3 ^a	96.7 ± 1.0 ^{abc}	13.0 ± 0.1 ^a
D1M00	54.8 ± 0.2 ^a	165.1 ± 0.2 ^{abc}	94.9 ± 0.6 ^{de}	16.1 ± 0.0^b
D1M05	54.6 ± 0.4 ^a	165.6 ± 0.4 ^a	95.8 ± 0.5 ^{ef}	11.2 ± 0.2 ^c
D1M10	53.0 ± 0.1 ^b	165.1 ± 0.2 ^{abc}	94.4 ± 0.7 ^d	11.4 ± 0.4 ^c
D1M20	51.1 ± 0.1 ^c	164.7 ± 0.4 ^{bc}	94.5 ± 0.5 ^d	10.4 ± 0.2 ^d
D1M30	49.9 ± 0.1 ^d	163.9 ± 0.2 ^{de}	93.2 ± 0.4 ^g	10.2 ± 0.2 ^d
D2M00	53.8 ± 0.5 ^e	165.3 ± 0.5 ^{ac}	94.8 ± 0.6 ^{de}	15.1 ± 0.1^e
D2M05	53.8 ± 0.4 ^e	165.8 ± 0.4 ^a	97.3 ± 0.3 ^{bc}	9.7 ± 0.0 ^f
D2M10	53.0 ± 0.3 ^b	165.6 ± 0.6 ^a	97.8 ± 0.5 ^c	9.5 ± 0.1 ^f
D2M20	51.0 ± 0.4 ^c	164.5 ± 0.6 ^{bd}	96.2 ± 0.5 ^{ab}	7.4 ± 0.3 ^e
D2M30	48.3 ± 0.6 ^f	163.2 ± 0.2 ^e	94.3 ± 0.4 ^{dg}	7.2 ± 0.0 ^e

Values in the same column with different superscript letters are different at $\alpha = 0.05$.

Figure 4.6 a and b show the thermal stability of the PLLA-g-MAH samples. The onset decomposition temperature of neat PLLA was found to be around 290 °C. The decomposition temperature of the samples was affected by the addition of MAH. Moreover, the weight loss started at around 105 ~ 110 °C for all MAH grafted samples, and this could be attributed to the decomposition of residual moisture in the samples. The decomposition temperatures of DIM05 and D2M05 samples were far below that of neat PLA. This could be correlated with the lower

molecular weight of the two samples. Samples with 0.2 phr DCP showed greater reduction in thermal stability due to their overall lower molecular weight as compared to samples with 0.1 phr of DCP.

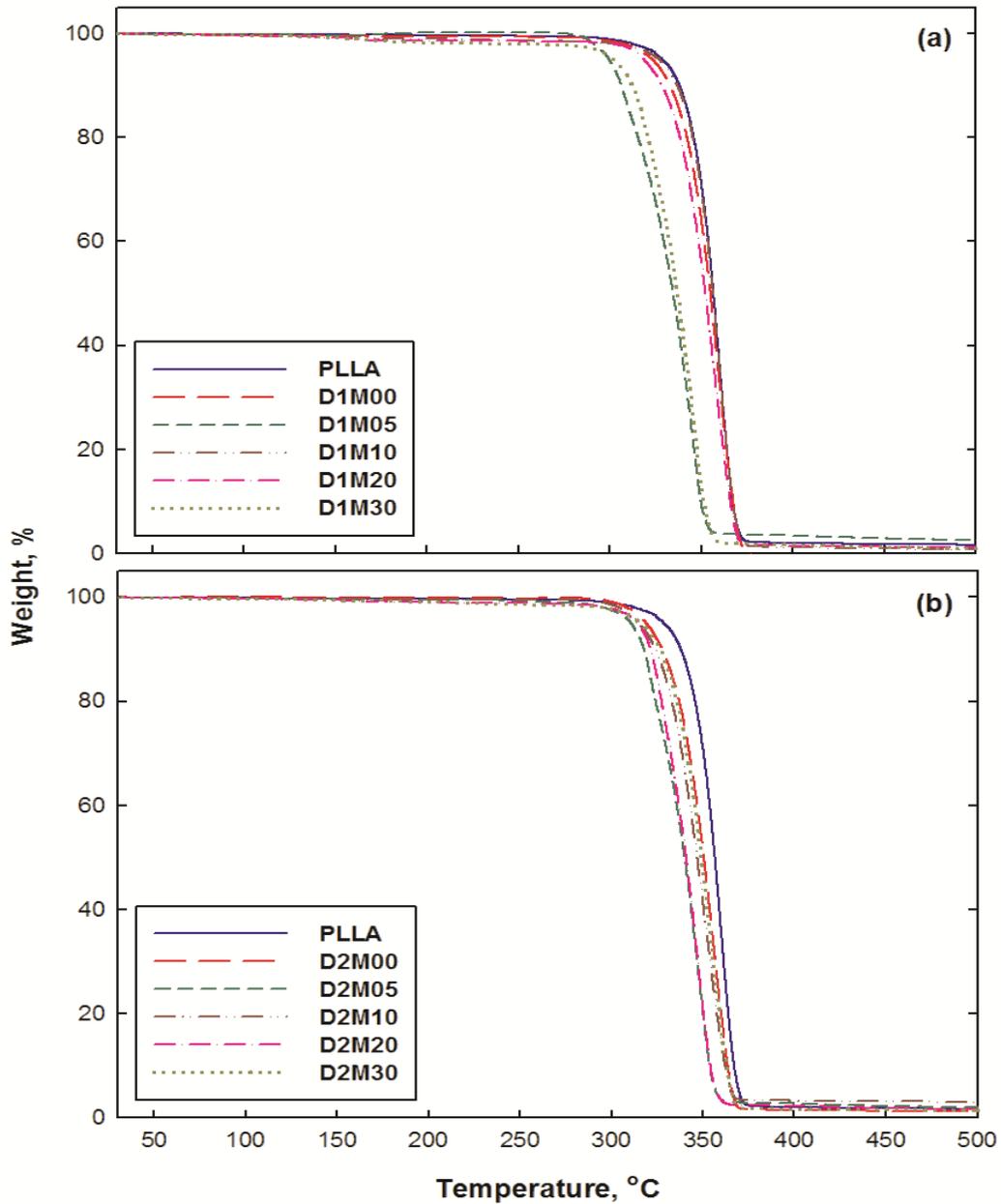


Figure 4.6 TGA thermograms of neat PLLA and maleated PLLA with different DCP contents: (a) 0.1 phr and (b) 0.2 phr.

4.3.4 Thermo-mechanical and mechanical properties

Figure 4.7 shows the storage modulus (G') of neat PLLA and maleated PLLA samples as a function of temperature. PLLA samples with only DCP added (D1M00 and D2M00) showed considerable decrease in G' . In the presence of a radical initiator (DCP), PLLA could exhibit not only hydrogen radical abstraction and light crosslinking due to radical coupling, but also chain scission resulting in chain branching[35].

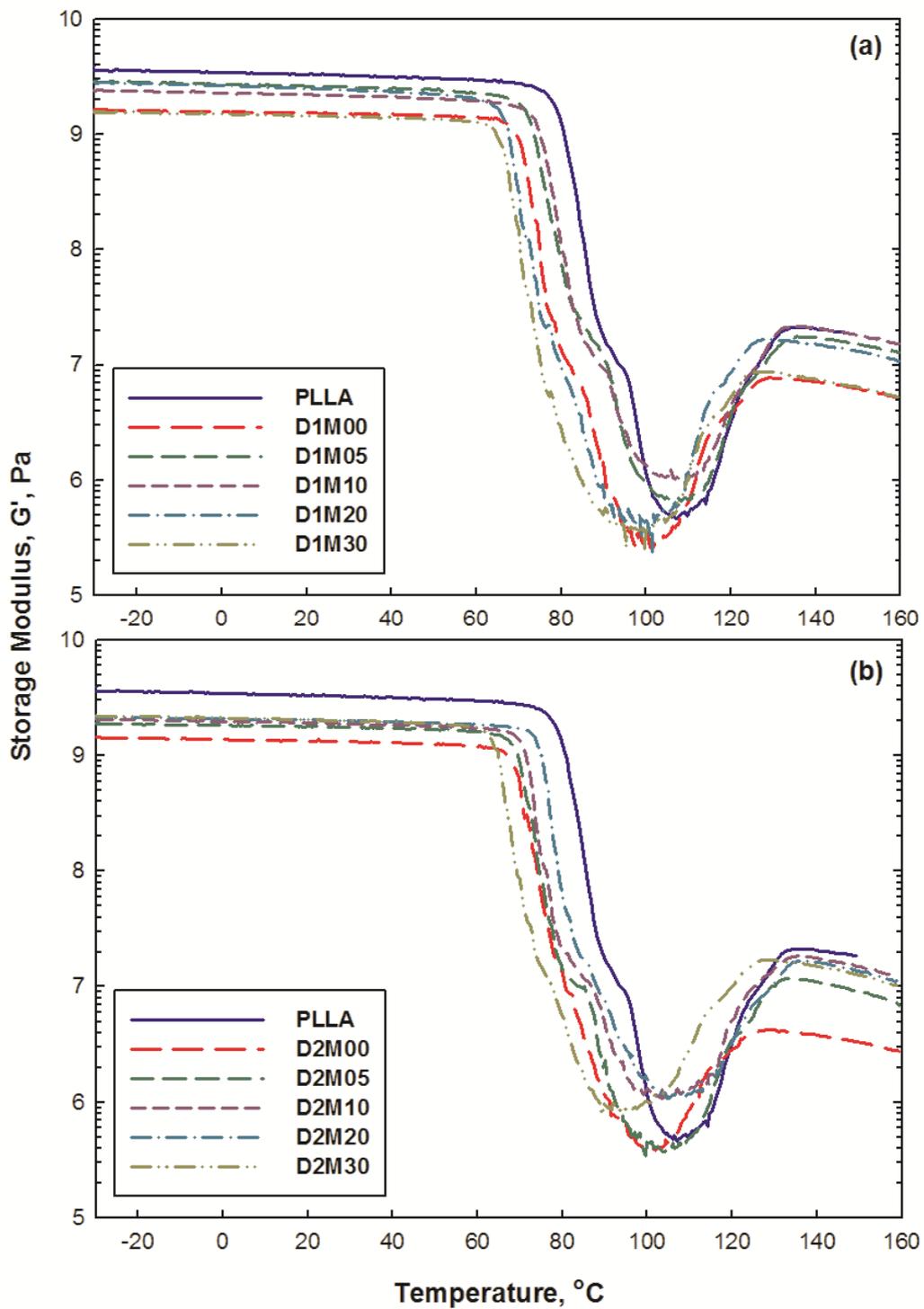
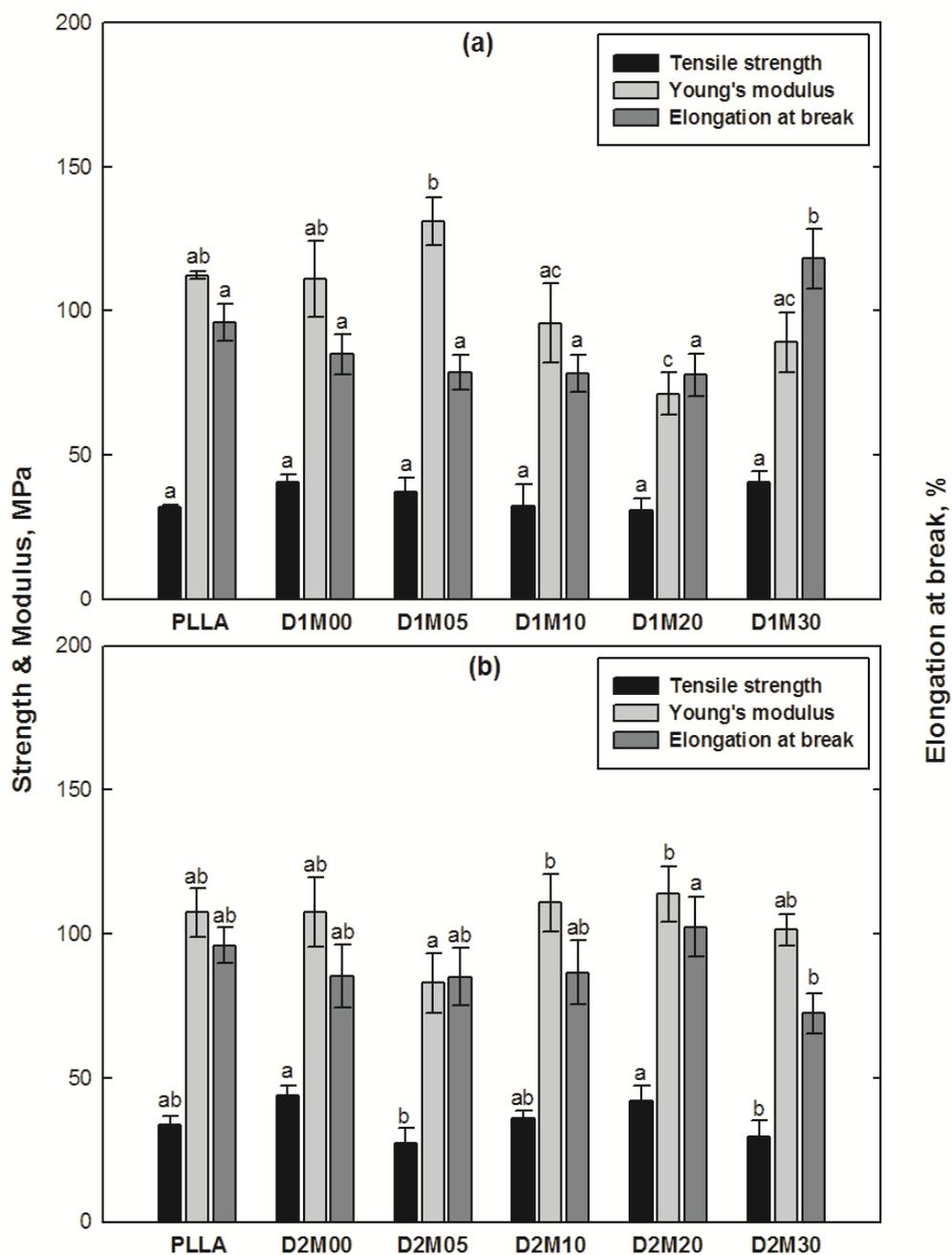


Figure 4.7 DMA results of neat PLLA and maleated PLLA with different DCP contents: (a) 0.1 phr and (b) 0.2 phr.

These reactions could weaken the chain restrictions of PLLA, so more chain vibration and short range rotational motions causing decreased G' could occur[36]. As seen in Table 4.3, samples without MAH, D1M00 and D2M00, had higher crystallinity than neat PLLA. If the chain restriction of PLLA is weakened, it could be assumed that the chance of molecular rearrangement of PLLA could increase, resulting in higher crystallinity. As the MAH was introduced into PLLA, the G' increased again, but not as much as neat PLLA. It can be assumed that increasing the amount of reactive MAH increased branching reactions, thus increasing chain restrictions of PLLA. The onset temperature of cold crystallization of samples (D1M00, D1M20, D1M30, D2M00, D2M05, and D2M30) shifted to a lower temperature compared to neat PLLA. The addition of MAH in PLLA enhanced the cold crystallization ability of PLLA. A decrease in T_g and an enhancement of the cold crystallization process due to the addition of plasticizing agents were previously observed for plasticized PLLA[37, 38]. The tensile strength, modulus, and elongation at break of maleated PLA samples are shown in Figure 8. The introduction of MAH onto PLLA resulted in only minor differences between the mechanical properties of the samples.



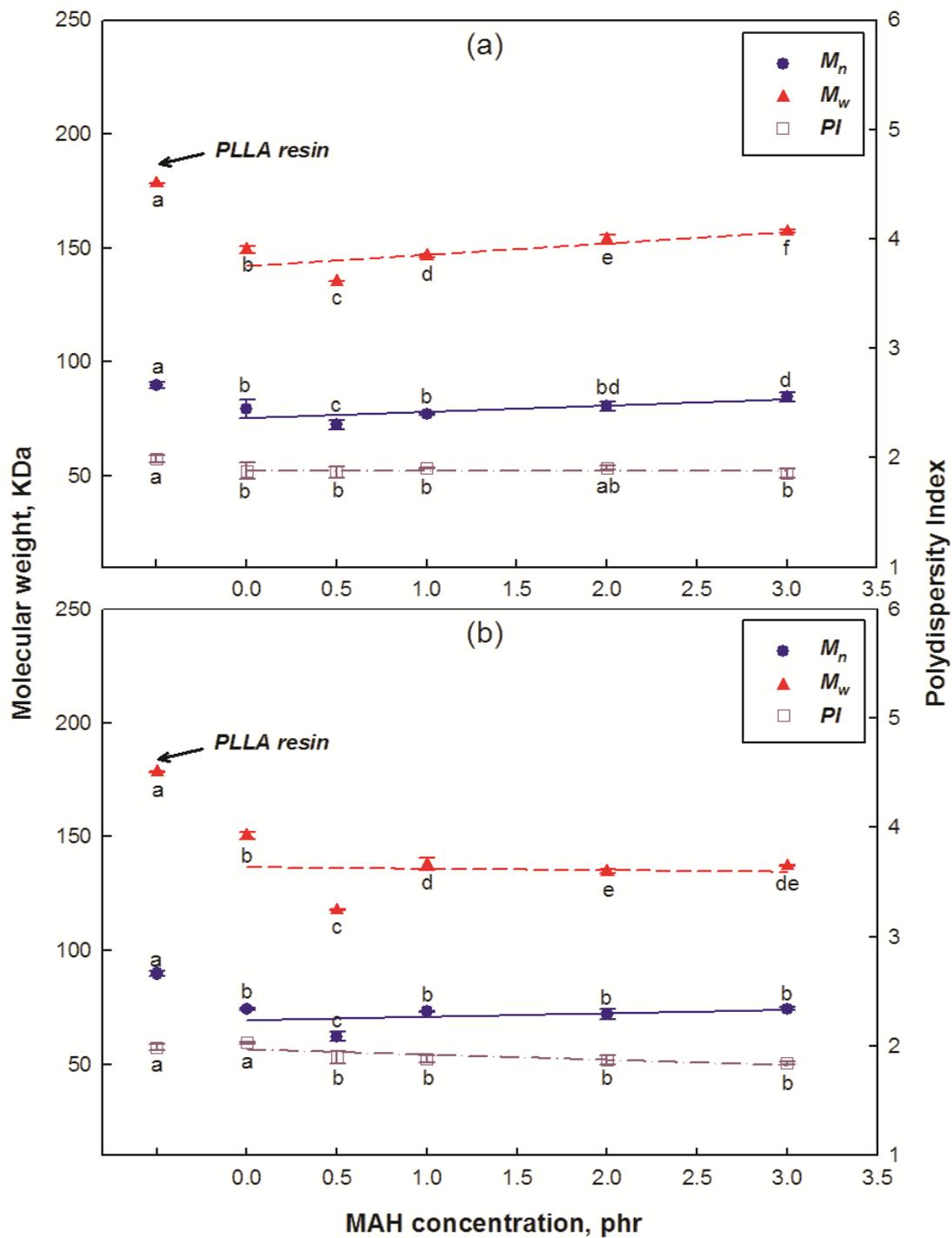
Values in the same color bar with different letters are significantly different at $\alpha = 0.05$.

Figure 4.8 Tensile strength, Young's modulus, and elongation at break of PLLA and maleated PLLA with different DCP contents: (a) 0.1 phr and (b) 0.2 phr.

4.3.5 Molecular weight

Figure 4.9 shows a decrease in number and weight average molecular weights (M_n and M_w) of PLLA-g-MAH samples up to 0.5 phr of MAH while the polydispersity index (PI) remained stable with a little significant difference at both 0.1 and 0.2 phr DCP content.

This slight decrease of M_n and M_w could be attributed to formation of PLLA radicals due to introduction of DCP. In samples with more than 0.5 phr MAH, the MAH branching reaction and possible crosslinking reaction could occur. This could increase chain entanglements resulting in increase of molecular weight and slight decrease of MFI (Figure 4.10). This result can be partly correlated and explained by the reduction of the thermal stability of the samples with up to 0.5 phr MAH. An increase in thermal decomposition temperature was found for samples with more than 0.5 phr of MAH. Similar results have been reported by Carson *et al.* where maleated samples showed decreased thermal stability compared to neat PLLA[6].



Values in the same color with different letters are significantly different at $\alpha = 0.05$.

Figure 4.9 M_n , M_w , and PI of maleated PLLA with different DCP contents: (a) 0.1 phr and (b) 0.2 phr.

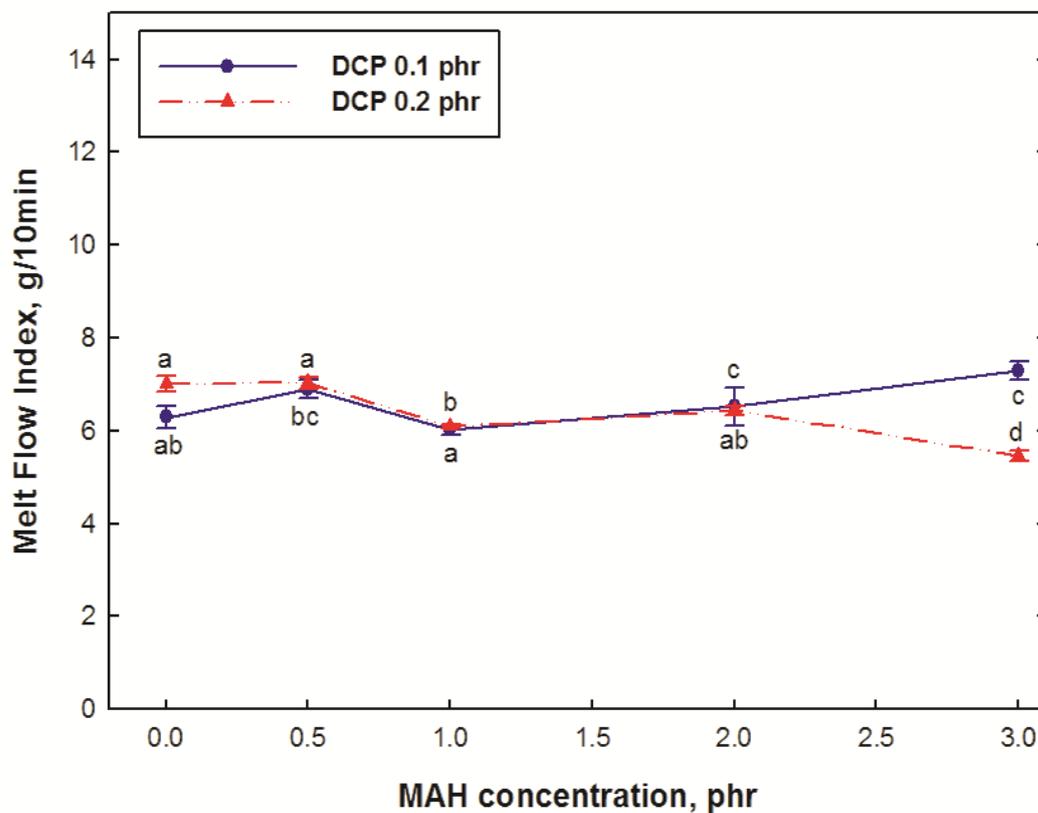


Figure 4.10 MFI of maleated PLLA with different DCP contents

4.4 Conclusions

A grafting reaction was successfully achieved and confirmed by both FT-IR and $^1\text{H-NMR}$ of MAH onto PLLA. Introduction of a small amount of MAH had a great effect on reducing gel content by increasing grafting yield. The T_g and % X_c were significantly decreased by the addition of MAH due to chain branching resulting from the grafting reaction between PLLA and MAH resulting in an increase in the segmental mobility of the PLLA chain. Reduced thermal stability of the maleated PLLA as compared to neat PLLA was found, and this result was correlated with molecular weight decrease of the PLLA-g-MAH samples. The thermal stability

of the samples was influenced by the MAH content while the mechanical properties were not affected much by the grafting reactions.

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4.5 References

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CHAPTER V

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CHAPTER V

Effect of Maleic Anhydride Grafting Reaction on the Physical and Mechanical Properties of Poly(L-lactic acid)/Starch Blends

Abstract

Maleic anhydride (MAH) was grafted onto both poly(L-lactic acid) (PLLA) and starch in an internal mixer in the presence of dicumyl peroxide (DCP) in a one step reactive compatibilization process. The effect of maleation of MAH on physical and mechanical properties, and morphology of PLLA/starch blends was assessed. The onset decomposition temperature of PLLA/starch blends decreased as the starch content increased due to the lower thermal stability of starch, and the low effect of the maleation reaction on the thermal stability of the PLLA/starch blends. PLLA/starch blends with grafted MAH showed significant decrease of T_g due to the plasticizing effect of MAH. The percent crystallinity (X_c) for PLLA/starch blends without reactive compatibilization increased as starch content increased due to the nucleation effect of starch. It appears that reactive compatibilization by grafting MAH onto PLLA and starch competed with crosslinking reactions of PLLA in the presence of DCP resulting in reduction of X_c of PLLA/starch blends. Reactive compatibilization resulted in increase of E' of PLLA/starch blends indicating that compatibility between two phases increased by reactive compatibilizer. Good interfacial adhesion between PLLA and starch was found in the blends.

5.1 Introduction

Melt blending is a common technique for polymer modification or for blending of two or more polymers since it uses a conventional processing method with low cost. Blending poly(lactic acid) (PLA) with non-renewable based polymers has been widely studied to improve the mechanical properties of PLA[1-4]. Wang *et al.* investigated PLA/LDPE blends, and reported that the crystallinity of PLA had a significant effect on the toughness of the blends[1]. It was also reported that blending PLA and poly propylene (PP) improved the resistance of PLA to hydrolysis and the dyeability of PLA; reducing also the biodegradability[5]. Yoo *et al.* investigated the effect of adding maleated PP (3 phr (parts per hundred resins)) on PP/PLA (80/20) blends. They showed that the addition of compatibilizer on the PP/PLA blends greatly improved tensile strength. They also showed that PP/PLA blends compatibilized with styrene-ethylene-butylene-styrene-grafted-maleic anhydride showed decreased tensile strength; but they suggested that it could effectively be used as an impact modifier to improve the impact strength of the PP/PLA (80/20) blends[6]. Mohamed *et al.* found that the incorporation of polystyrene (PS) in PLA resulted in thermal stabilization of the blends although the final blends were immiscible, confirmed by two independent T_g s[7].

Blending of PLA with renewable polymers has also extensively been investigated to enhance PLA's mechanical properties without compromising its biodegradability and compostability. Poly(3-hydroxybutyrate)-co-(3-hydroxyvalerate) (PHBV) was blended with PLA by solvent casting. PLA and PHBV blends showed partial molecular interaction although phase separation was found, indicating that the blends were not compatible[8]. Improved impact toughness for PLA/poly(3-hydroxyalkanoate) (PHA) blends was also reported, and the addition of epoxy groups in the PHA phase could be unstable and interact with the hydroxyl groups of

PLA resulting in higher interaction between phases, as confirmed from morphological observations[9]. The addition of ethylene oxide and propylene oxide surfactant was found to significantly improve the toughness of PLLA/PDLLA blends, and increased the elongation at break in PLLA/PCL blends[10]. The effect of crosslinking with dicumyl peroxide (DCP) on PLA/PCL blends was also studied, and it was found that blends with small amounts of DCP showed high compatibility due to increased interfacial adhesion[11]. Suyatma *et al.* found phase separation in PLA/chitosan blends prepared from solution casting, concluding that the blends were incompatible. However, they reported that blending chitosan with PLA could enhance the water vapor barrier property and hydrophobicity of chitosan[12]. PLA/starch blends were also investigated by several research groups. Ke *et al.* reported that water absorption of the PLA/starch blends containing above 50% amylose improved the water resistance of blends without compromising the mechanical properties[13]. They also investigated the crystallization behavior of PLA/starch blends and found that 1% starch effectively increased the crystallization rate[14].

Reactive compatibilization is one of the main methods to improve compatibility by inducing a chemical reaction between two polymers during their blending, thus providing direct interaction between the polymers[15-17]. In a reactive compatibilization process, small dispersed phases (or domains) are formed, which could enhance the interfacial adhesion of two immiscible polymers by reducing the interfacial tension between them. In this way, the phase morphology of blends can be stabilized by preventing the coalescence of dispersed domains. The improved interfacial adhesion also results in better mechanical properties[16, 17]. Kalambur and Rizvi investigated starch and PCL nanocomposites using Fenton's reagent to get crosslinking between oxidized and PCL by reactive extrusion, and reported that the elongation of starch-PCL

nanocomposites was comparable to that of 100% polyester while the strength and modulus remained the same as those in starch–PCL composites without crosslinking[18].

Maleic anhydride (MAH) is one of the most widely used reactive compatibilizers due to its good chemical reactivity. It also has low toxicity and low potential to polymerize itself under free radical grafting conditions[19]. Many researchers have reported that MAH can be easily grafted (-g-) onto polyolefins in the presence of an initiator such as 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane (Luperox 101, L101) and dicumyl peroxide (DCP) during melt processing[20-23].

In the case of PLA and starch, MAH can functionalize both polymers since PLA contains carboxyl and hydroxyl end groups as functional groups, and starch has hydroxyl groups as its main functional group[24]. MAH with a radical initiator, L101 for the PLA/wheat starch blends, was reported to improve the interfacial adhesion between phases, and to produce higher tensile strength and elongation at break in 55/45 PLA/starch blends with 1% MAH[25]. Orozco *et al.* functionalized PLA with MAH (PLA-g-MAH) using DCP as an initiator by a grafting process, and applied PLA-g-MAH to PLA/Starch blends. All compatibilized PLA/starch blends showed better interfacial adhesion, attributed to the chemical reaction between the hydroxyl groups and anhydride groups[26]. The addition of 3 and 5 phr PLA-g-MA to the PLA/wheat straw composites resulted in significant improvements in tensile strength (20%) and flexural strength (14%) indicating improved interfacial adhesion between the fiber and PLA[27].

Numerous approaches have been studied to improve interfacial adhesion between PLA and starch or thermoplastic starch. However, there has been scarce investigation of one-step reactive compatibilization. In this study, we prepared PLLA/corn starch blends without and with one-step reactive compatibilization process of MAH in the presence of DCP radical initiator to

improve PLLA properties. The effect of one-step reactive compatibilization on the physical and thermal properties on PLLA/starch blend was investigated, and feasibility of MAH as a reactive compatibilizer in PLLA/starch blends was assessed.

5.2 Experimental

5.2.1 Materials

PLLA resin, 4042D grade (94% L-lactic acid) (NatureWorks LLC, MN) and corn starch (Daesang, Seoul) (inherent moisture content of 11%) were used. PLLA was dried in a vacuum oven at 60 °C for 24 hours, and starch was dried in a vacuum oven at 120 °C for 3 hours in order to remove residual moisture. Dicumyl peroxide (DCP) and maleic anhydride (MAH) (briquettes, 99%) obtained from Sigma-Aldrich (St. Louis, MO, USA) were used for radical initiator and grafting reaction, respectively. All chemicals were used as received.

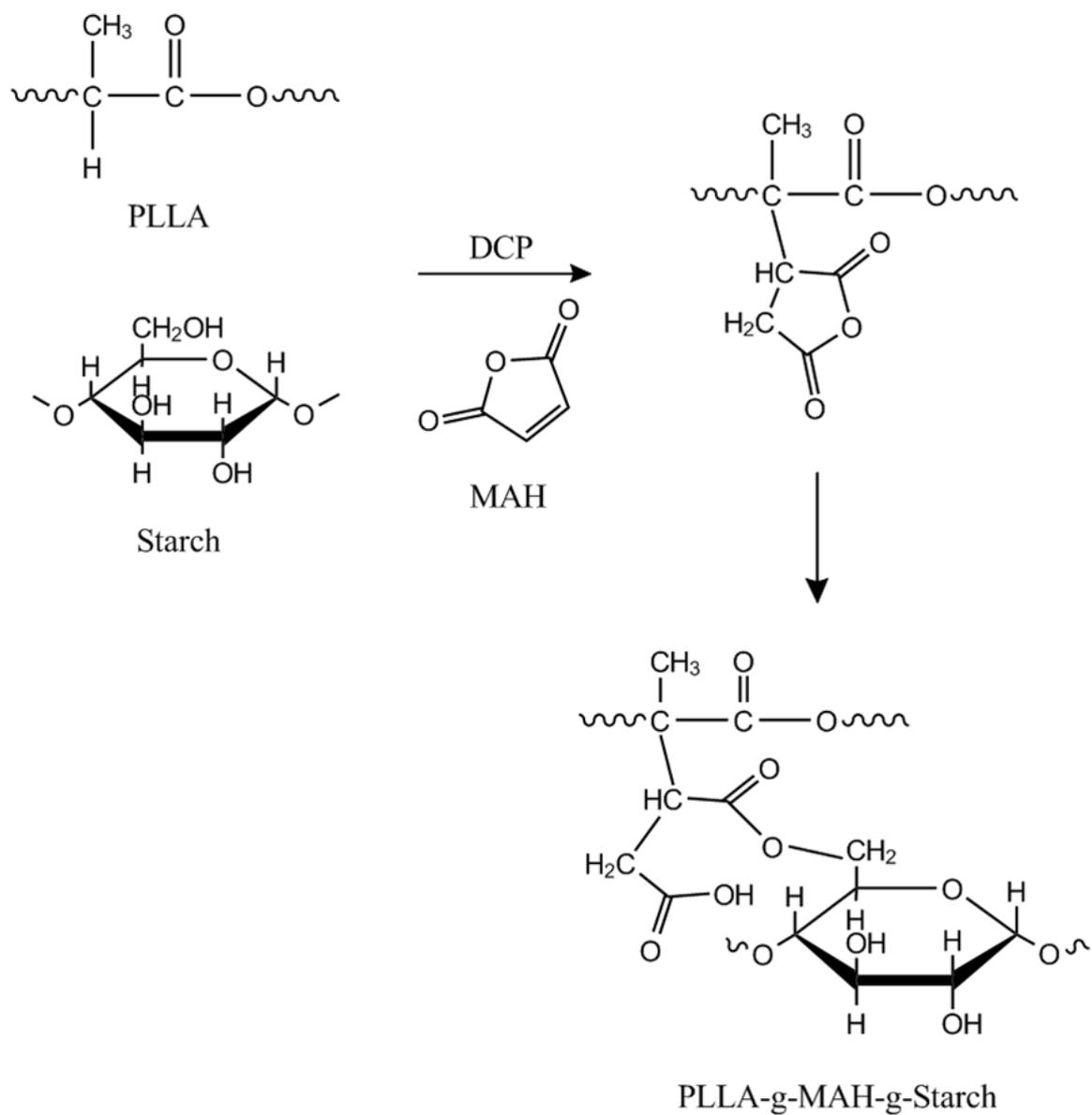
5.2.2 Preparation of PLLA/starch blends

The PLLA/starch blends were prepared in a Brabender Plasticoder PLE 331 (Brabender, Duisburg, Germany) at 190°C with a rotor speed of 60 rpm, and the total mixing time was fixed at 10 min. The blend ratios used in this study are presented in Table 5.1 and denoted by PS0, PS10, PS20, and PS30. The numerical values denote the weight percentage (wt.-%) of starch in the blends. The nominal concentrations of DCP and MAH were previously determined as the optimal conditions for PLLA grafting[28]. The presence of DCP and MAH is indicated with a D at the end of the blend ratio designation (i.e., PS10D, PS20D, and PS30D)

Table 5.1 Nominal blend ratio of PLLA/starch blends

Sample	PLLA, wt.-%	Starch, wt.-%	DCP, phr	MAH, phr
PS0	100	0		
PS10	90	10	0.1	2
PS20	80	20		
PS30	70	30		

The PLLA and starch were first melted in the Brabender for 2 min, and then DCP and MAH were added and mixed for 8 min. The PLLA/starch blend sample was then ground into small pieces with a grinder, DHG14 (Daeheung Tech, Daegu, Korea). The tentative chemical reaction between PLLA, starch, and MAH is presented in Scheme 5.1 as previously reported by Zhang *et al.* [25].



Scheme 5.1 Chemical reaction of PLLA, MAH, and Starch, modified from Zhang *et al.*

The prepared PLLA/starch blends were converted to 150 ~ 200 μm films by compression molding in a hydraulic laboratory press model 3925 (Carver, Wabash, IN) with a pressure of $150\text{Kg}\cdot\text{cm}^{-2}$ for 3 min at 200 $^{\circ}\text{C}$.

5.2.3 Characterizations

5.2.3.1 Thermal Analyses

Thermal properties such as the glass transition temperature (T_g), melting temperature (T_m), and percent crystallinity (X_c) were determined with a differential scanning calorimeter (DSC) (DiamondTM DSC, Perkin-Elmer, Waltham, MA, USA). The analyses were carried out under a nitrogen atmosphere between 20 and 220 °C at a heating rate of 5 °C·min⁻¹, and were analyzed by Diamond Analysis software. The heat of fusion (93.1 J·g⁻¹)[29] for 100 % PLLA was used to determine the percent crystallinity by the following equation (1)[30].

$$x_c(\%) = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^c \cdot w_f} \times 100 \quad (1)$$

where ΔH_m is enthalpy of fusion, ΔH_c is the enthalpy of cold crystallization of the PLLA/starch blends, and ΔH_m^c is enthalpy of fusion of pure crystalline PLA; $\Delta H_m^c = 93.1 \text{ J} \cdot \text{g}^{-1}$ [29]. w_f is the weight fraction of PLLA in the blends.

Thermal gravimetric analysis (TGA) (Q600, TA Instruments, New Castle, DE, USA) was used to assess the thermal stability of the PLLA/starch blend samples. The measurements were carried out under a nitrogen atmosphere up to 800 °C with a heating rate of 10 °C·min⁻¹.

5.2.3.2 Thermo-mechanical properties

Dynamic mechanical analysis (DMA) of the PLLA/starch blend film samples was performed on a Triton Technology DMA (TTDMA) from Triton Technology Ltd., Keyworth, UK. Samples with a width of 6.0 – 6.5 mm and a length of 8 – 10 mm were tested in the tension mode. The sample dimensions were entered based on the mean value of 5 points. The storage modulus, E' and $\tan \delta$ were measured at a heating rate of $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ and a temperature range of 0 to $180\text{ }^{\circ}\text{C}$ with a frequency of 1 Hz.

5.2.3.3 Mechanical properties

Mechanical properties such as tensile strength, Young's modulus, and elongation at break were assessed by a Universal Test Machine (UTM) (Instron 4465, Instron, Canton, MA) according to ASTM D 882-11. The samples were cut into 1×8 cm strips and conditioned at 23°C and 50% RH for 24 hr before testing. Five specimens were tested at a crosshead speed of $10\text{ mm}\cdot\text{min}^{-1}$ with a 4 cm initial gap separation.

5.2.3.4 Morphological properties

The morphology of the PLLA/starch blend samples was investigated using a field emission scanning electron microscope (FE-SEM, JSM 6706F, JEOL Ltd. Tokyo, Japan). The molded samples were fractured after freezing in liquid nitrogen to prevent deformation during fracture. The fracture surfaces were sputter coated with gold. In addition, the morphological structure of starch extracted PLLA/starch blends was studied. The fractured surface was immersed in boiling water for 60 min to remove the starch phase, and completely dried at $60\text{ }^{\circ}\text{C}$ for 24 hrs[31]. PLLA can be hydrolyzed at 180 ° to $350\text{ }^{\circ}\text{C}$ for up to 30 min, obtaining L-lactic acid as the final

product[32]. This phase extraction was conducted at much lower temperature. The obtained PLLA micrograph showed no evidence of such hydrolysis; furthermore, Zhang and Sun successfully used this methodology to previously reported PLA morphological blends[31].

5.2.3.5 Molecular weight

The molecular weight of PLLA/starch blends was determined with a gel permeation chromatograph (GPC) (Alliance GPCV 2000 system, Waters, Milford, MA, US). Twenty mg of PLLA/starch blend samples were dissolved in 10 mL of chloroform (CHCl₃, 99.9%) (Merck, Darmstadt, Germany) and 50 µL of each sample solution was injected into the GPC. The GPC was equipped with an isocratic pump, an autosampler, a series of 2 columns (Waters Styragel HR5E and HR4E), and a refractive index detector. The flow rate was 1 mL·min⁻¹, runtime was 40 min, and temperature was 35 °C. The Mark-Houwink constants $K = 0.0131 \text{ (mL}\cdot\text{g}^{-1})$ and $a = 0.759$ for chloroform at 30 °C for dilute PLLA solution were used[33].

5.2.3.6 Statistical Analysis

Statistical analyses of the PLLA/starch blends data were performed with SPSS software (SPSS, Inc., Chicago, IL). Data was pull together and analyzed as one-way analysis of variance using the General Linear Model procedure and Tukey's honestly significant difference (HSD) tests were used to determine significant differences ($P < 0.05$).

5.3 Results and Discussion

5.3.1 Thermal Analyses

Figure 5.1 (a) shows the thermal stability of PLLA/starch blends. Starch showed initial weight loss at around 100 °C due to water evaporation, and started to decompose around 290 °C. The moisture content in starch was found to be around 12 % wt. Figure 5.1 also shows that the onset decomposition temperature (T_d) of PLLA/starch blends decreased as starch content increased due to the lower thermal stability of starch as compared to neat PLLA. PS10, PS20 and PS30 had T_d values of 275, 265, and 263 °C, respectively, indicating that the reduction of T_d was not linear.

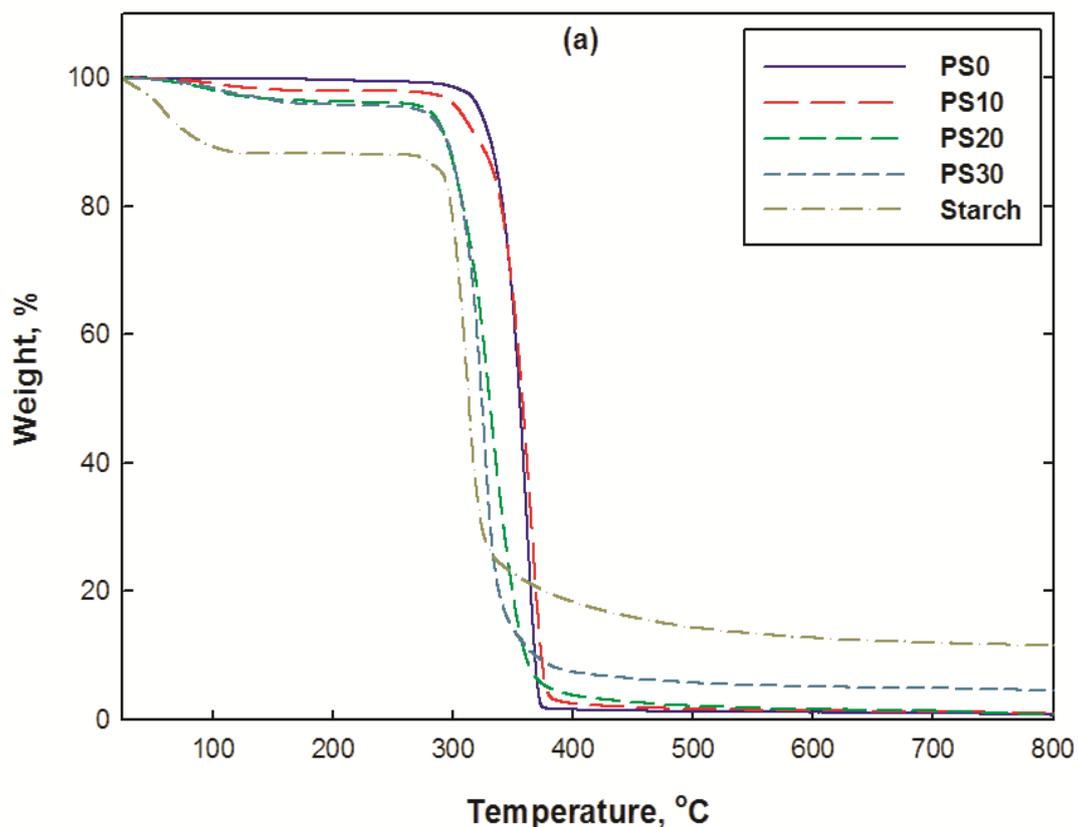
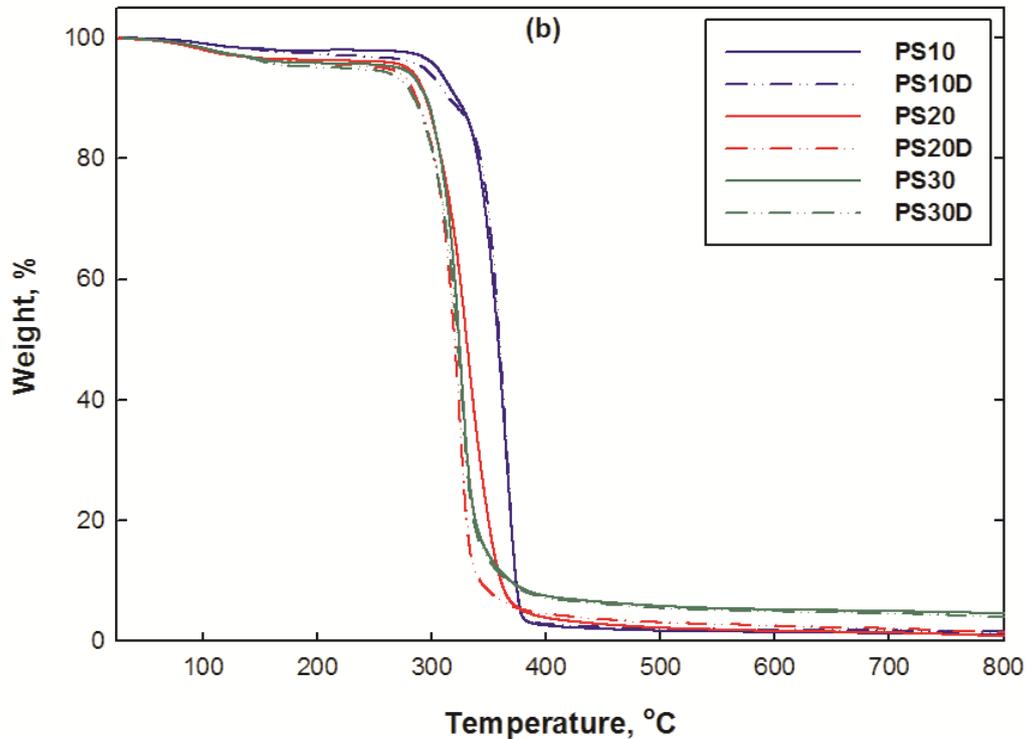


Figure 5.1 TGA curves of PLLA/starch blend samples (a) without reactive compatibilization and (b) with reactive compatibilization

Figure 5.1 (cont'd)



The grafting reaction did not significantly influence the onset decomposition temperature of the PLLA/starch blends, indicating that the maleation reaction had little effect on the thermal stability of the PLLA/starch blends (Figure 5.1 b). Orozco *et al.* also reported that the decomposition temperature of PLA was not affected by the grafting reaction of MAH on PLA when producing PLA/starch blends with DCP as initiator[26].

The DSC characteristics of the PLLA/starch blends without and with reactive compatibilization are listed in Table 5.2. The T_g of PLLA/starch blends without MAH did not show large variation due to the addition of starch although there were statistically significant differences. However, the T_g and T_m of PLLA/starch blends with reactive compatibilization

decreased significantly as compared PLLA/starch blends without reactive compatibilization. This could be attributed to the plasticizing effect of the lower M_w PLLA-g-MAH created during the grafting reaction. Jang *et al.*[34] found a decrease of T_g in PLA/starch blends, attributing this to the plasticizing effect of MAH. The T_c of the PLLA/starch blends without and with reactive compatibilization decreased with starch contents. This could be correlated to increased polymer chain mobility resulting in lower T_c and/or the nucleation effect of the low M_w of PLLA-g-MAH.

Table 5.2 Thermal characteristics of PLLA/starch blends

Sample	T_g	T_c	T_m	X_c , %
PS0	58.3 ± 0.1^a	113.0 ± 0.3^a	155.5 ± 0.0^a	1.9 ± 0.5^a
PS10	$57.2 \pm 0.1^{b,1}$	$111.4 \pm 0.3^{b,1}$	$153.5 \pm 0.3^{b,1}$	$4.2 \pm 0.1^{b,1}$
PS20	$56.8 \pm 0.2^{c,12}$	$104.9 \pm 0.5^{c,2}$	$152.1 \pm 0.0^{c,2}$	$9.9 \pm 0.2^{c,2}$
PS30	$56.2 \pm 0.0^{d,2}$	$102.0 \pm 0.1^{d,3}$	$151.4 \pm 0.1^{d,34}$	$17.0 \pm 0.7^{d,3}$
PS10D	51.4 ± 0.0^3	99.9 ± 0.0^4	151.6 ± 0.1^3	5.7 ± 0.8^4
PS20D	50.7 ± 0.9^3	102.9 ± 0.4^5	151.2 ± 0.2^4	2.3 ± 0.2^5
PS30D	51.0 ± 0.2^3	103.1 ± 0.2^5	150.6 ± 0.2^5	3.7 ± 0.2^1

Numbers followed by the same letter within a column are not significantly different using Tukey's HSD adjustment t-test with type I error (α) of 0.05.

Two distinct trends were found in the percent crystallinity (X_c). X_c for PLLA/starch blends increased from 1.9 to 17.0% as starch content increased due to the nucleation effect of starch on the blends. It was previously demonstrated that starch can act as a nucleating agent for crystallization of polymers[35]. The reactive compatibilization significantly decreased X_c for PS30D. This might be due to chain restriction induced by MAH branching and possible

crosslinking between PLLA chains. Tacamura *et al.* investigated the relationship between peroxide type and crosslinking of PLLA during reactive extrusion at constant radical content, and found that DCP results in crosslinking of PLLA at long extrusion times[36]. In addition, the double melting peak of PS0 and other blends as seen in Figure 5.2 might be attributed to melting of small and imperfect crystals resulting from recrystallization during melting[37]. These two endothermic peaks could be also related to the formation of α crystal which is most stable from α' crystal structure during recrystallization[38].

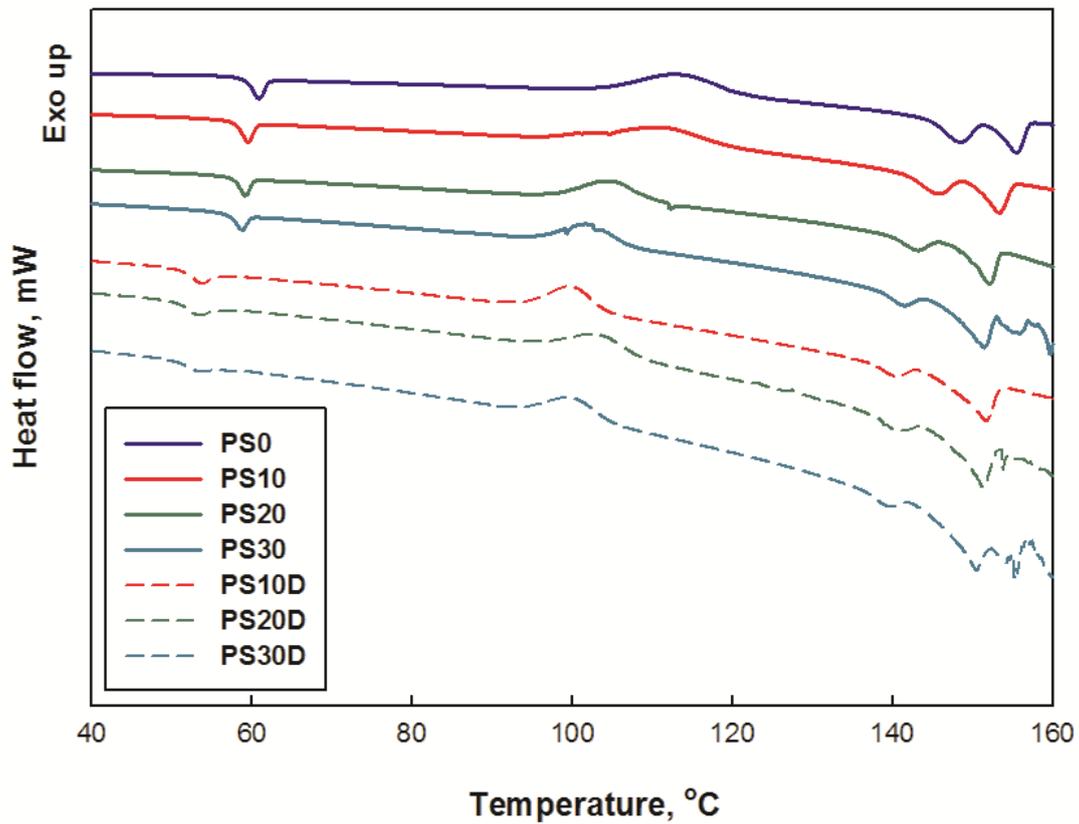


Figure 5.2 DSC thermograms of PLLA/starch blends

5.3.2 Thermo-mechanical properties

The storage modulus (E') and $\tan \delta$ of the PLLA/starch blends are presented in Figures 5.3, 5.4 and 5.5. The T_g (around 65°C) and T_{cc} (around 125°C) of PLLA are shown in Figure 3. The temperature difference for T_g between DSC and DMA could be due to the different techniques[39]. A higher T_g is reported by DMA due to the larger sample size and the mechanism for heat transfer. The addition of 10 and 20 wt.-% starch in PLLA decreased E' . However, when starch increased to 30 wt.-%, E' of PS30 increased again but not as much as neat PLA. This might be due to increased crystallinity of the PLLA/starch blends. It also can be seen that the incorporation of starch resulted in a broader and higher recrystallization peak indicating starch acted as a nucleating agent, as previously mentioned.

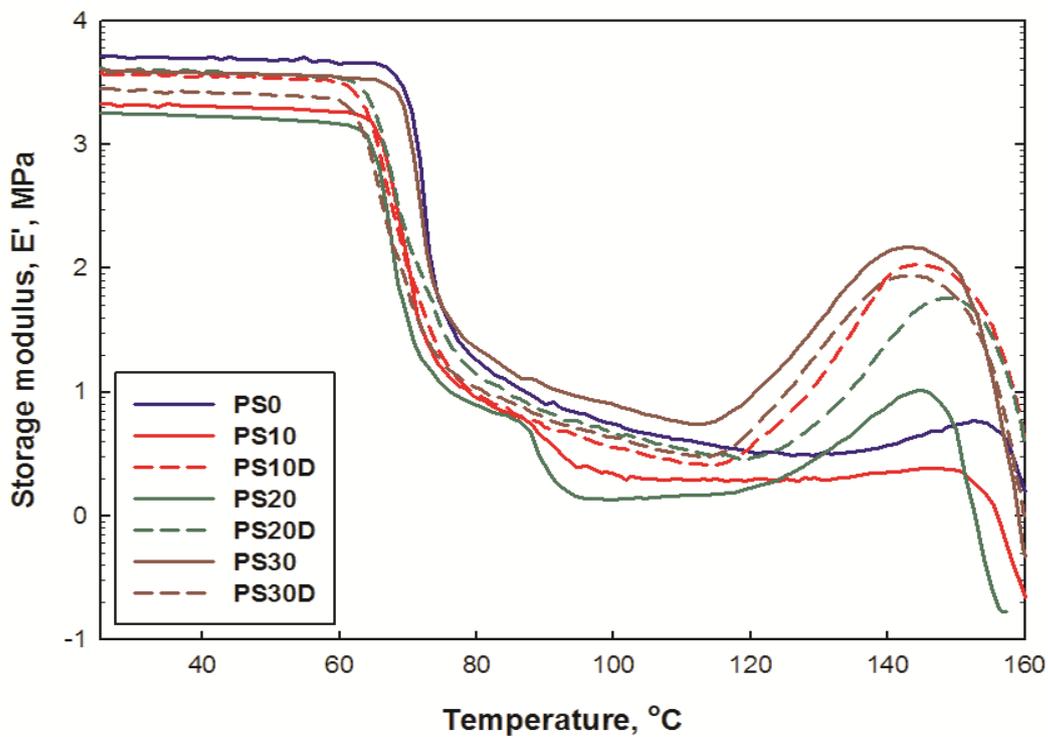


Figure 5.3 E' curve of PLLA/starch without and with reactive compatibilization

Figure 5.4 shows the plot of E' vs. starch content of PLLA/starch blends with and without reactive compatibilization at 40°C. E' starts to increase after 15% starch due to increase in stiffness and rigidity of PLLA/starch blends without reactive compatibilization. Below 15% starch, the plasticizing effect of starch predominates, resulting in reduced E' . Orozco *et al.* reported similar plasticizing effects on PLLA/starch blends, and E' increase was also observed at 15% starch in blends at 30°C[26]. In addition, reactive compatibilization resulted in increase of the E' of PLLA/starch blends indicating the compatibility between the two phases increased under presence of MAH and DCP. However, PS30D shows a decrease of E' , and it seems that the amount of DCP (0.1 phr) and MAH (2 phr) was not enough for acting as a compatibilizer at the 30% of starch content, so the plasticization effect of MAH and/or PLLA-g-MAH could be predominated.

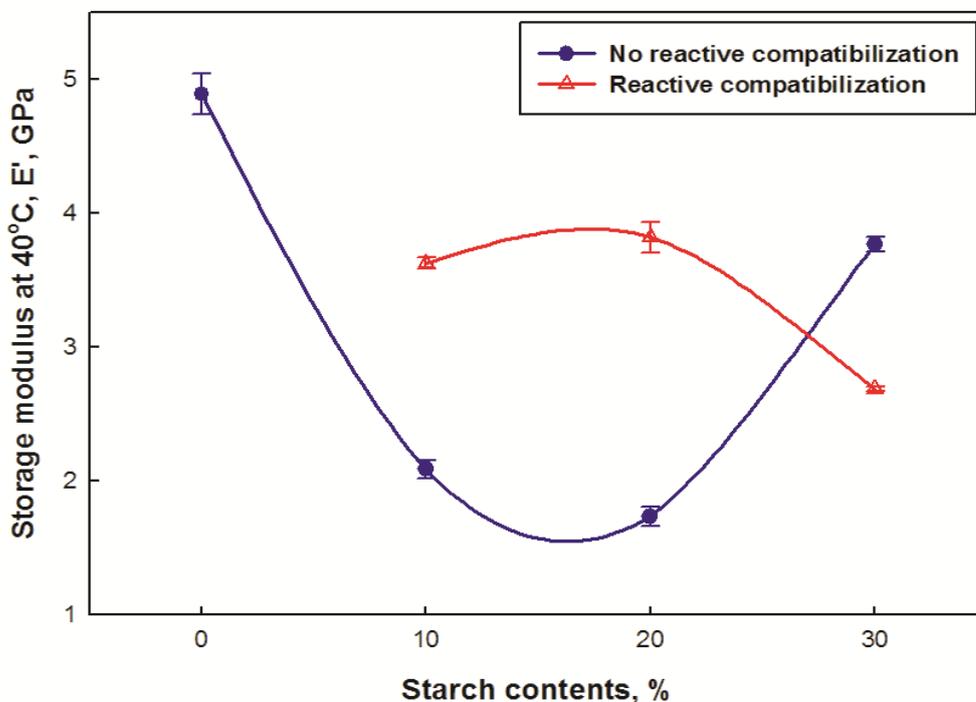


Figure 5.4 Storage modulus, E' as a function of starch content at 40°C of PLLA/starch blends

Zhang *et al.* reported that dioctyl maleate (DOM) could be acting as both compatibilizer and plasticizer in the PLA/starch blends. The compatibilization predominated at DOM concentration below 8%, while plasticization predominated at DOM concentration above 10%. The onset temperature of cold crystallization also decreased from 125 to 115°C as observed in the DSC thermogram[40]. As shown in Figure 5, PLLA/starch blends showed a lower damping peak, tan δ value, indicating that the addition of starch made the damping ability of blends lower as compared to PS0. In addition, the reactive compatibilization reduced the damping ability of starch in the blends.

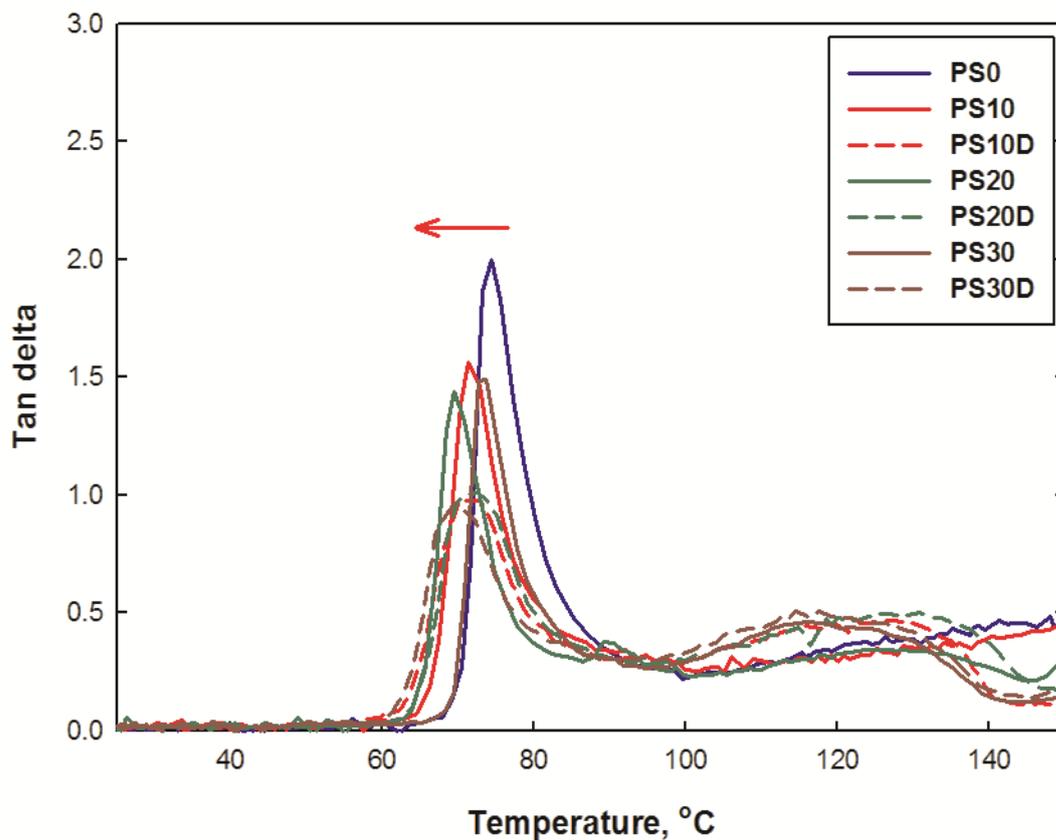


Figure 5.5 Tan δ curve of PLLA/starch without reactive compatibilization and with reactive compatibilization

5.3.3 Mechanical properties

The mechanical properties of the PLLA/starch blends with and without reactive compatibilization are presented in Table 5.3. The PLLA/starch blends had lower tensile strength than neat PLLA (PS0), and the tensile strength decreased as starch content increased due to the poor interfacial adhesion between the two phases. Reactive compatibilization improved the tensile strength indicating that the chemical linkage between MAH grafted onto PLLA and the hydroxyl groups of the starch improved interfacial adhesion between the two phases. The elongation of blends without reactive compatibilization slightly decreased as starch content increased. In maleated PLLA/starch blend samples, elongation at break was not affected up to 20% starch. Zhang *et al.* found MAH-g-PLA had increased tensile strength and modulus as compared to neat PLA. It was also found that the addition of MAH-g-PLA in PLA/starch blend resulted in slight decrease in elongation at break but tensile strength and modulus were kept same values as MAH-g-PLA[25] Wang *et al.* also reported reactive compatibilization has an effect on increasing 3.5% of elongation at break for starch/PLA blends (50:50) prepared by reactive extrusion[41].

Table 5.3 Mechanical Properties of PLLA/starch blends

Sample	Tensile strength MPa	Modulus GPa	Elongation at break %
PS0	56.3 ± 5.9 ^a	2.2 ± 0.1 ^a	3.6 ± 0.2 ^a
PS10	48.6 ± 1.9 ^{ab,1}	1.7 ± 0.1 ^{b,1}	3.2 ± 0.0 ^{b,1}
PS20	48.0 ± 4.3 ^{b,1,2}	1.9 ± 0.0 ^{b,1}	2.9 ± 0.2 ^{b,2}
PS30	35.9 ± 3.9 ^{c,3}	1.8 ± 0.2 ^{b,1}	2.1 ± 0.0 ^{c,3}
PS10D	53.4 ± 3.1 ¹	1.8 ± 0.1 ^{b,1}	3.4 ± 0.0 ⁴
PS20D	51.7 ± 3.4 ¹	2.3 ± 0.2 ^{a,2}	3.3 ± 0.0 ¹⁴
PS30D	41.9 ± 2.1 ^{2,3}	2.7 ± 0.0 ^{c,3}	2.6 ± 0.1 ⁵

Numbers followed by the same letter within a column are not significantly different using Tukey's HSD adjustment t-test with type I error (α) of 0.05.

5.3.4 Morphological properties

In general, the mechanical properties of polymer blends are highly dependent on the morphological structures of the blends. As shown in Figure 6 (a) – (b), clear edges and cavities were observed between the starch granules and the PLLA matrix, indicating poor interfacial adhesion. However, Figure 6 (d) – (f) shows improved interfacial adhesion between the PLLA and starch phases showing no clear differentiation. This could be attributed to the chemical linkage due to the reaction of the anhydride group grafted to PLLA and starch. In the case of blends with 30% starch, PS30, no clear cavities are observed, but there is still evidence of poor adhesion at the interfaces. Jang *et al.* investigated the phase morphology of PLA/starch blends with MAH as a compatibilizer in the presence of L101, and they found good interfacial adhesion between PLA and starch[41]. Orozco *et al.* reported PLA/starch blends having improved interfacial adhesion between PLA and starch phase by reactive compatibilization[26]. Orozco's result is in good agreement with the mechanical properties presented in Table 5.3.

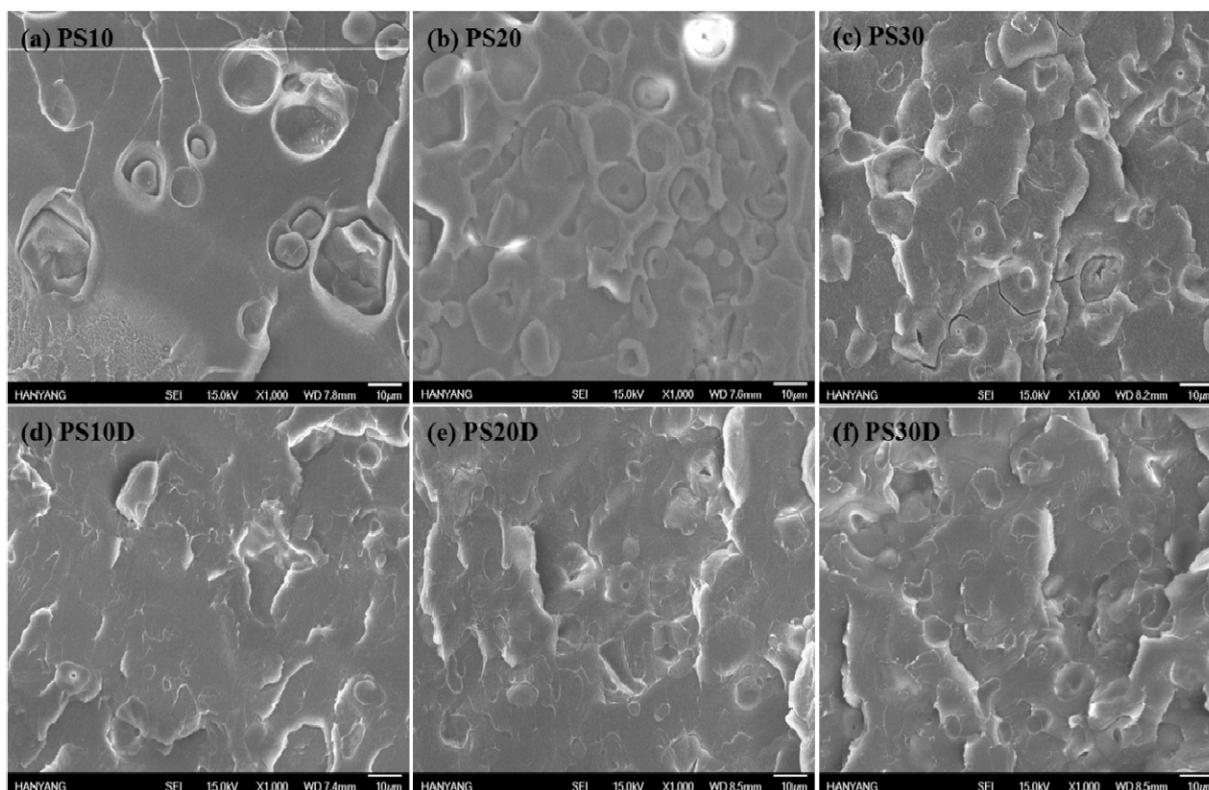


Figure 5.6 SEM micrographs of PLLA/starch blend samples

The fractured surface of all samples after extraction in boiling water showed a number of cavities where the starch granules had existed as domain in PLLA matrix indicating the starch were well dispersed in the PLLA matrix. In addition, the number of cavities increased as the starch content increased. The effect of reactive compatibilization was not clearly observed in Figure 5.7, but rough internal surface was observed in the PLLA/starch blends with grafting reaction (d) ~ (f) in Figure 8, which was not observed in the PLLA/starch blends without grafting reaction (a) ~ (c) indicating they had different phase morphology, and this could be correlated with interfacial adhesion. Zhang *et al.* also reported similar morphological observations after dissolving starch in boiling water, indicating that the sample surface had many holes where the starch granules had dissolved[31].

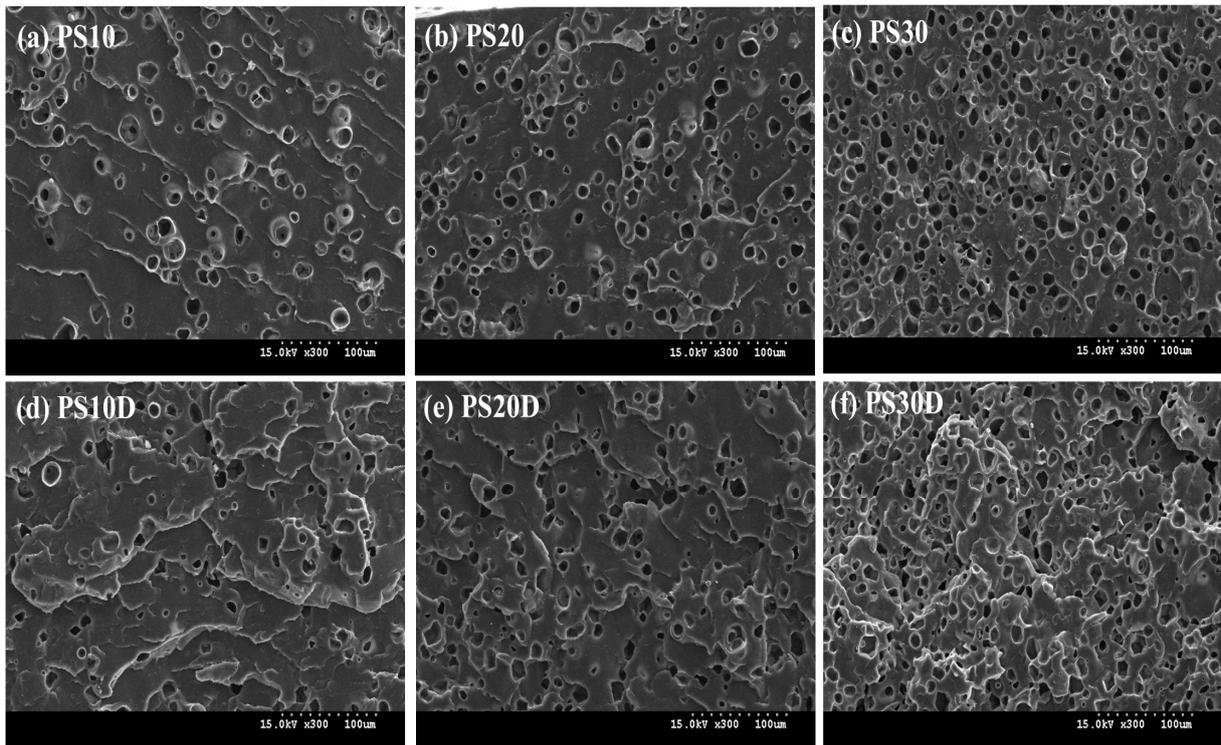


Figure 5.7 SEM micrographs of PLLA/starch blends after removing starch phase.

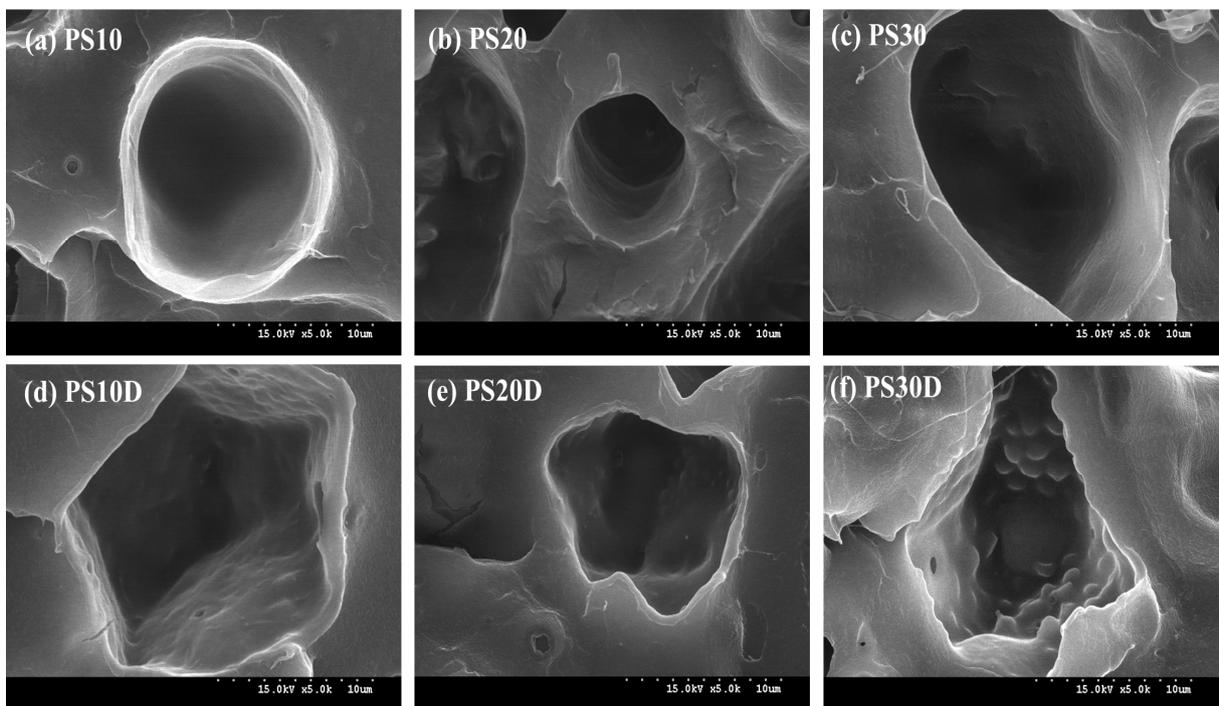
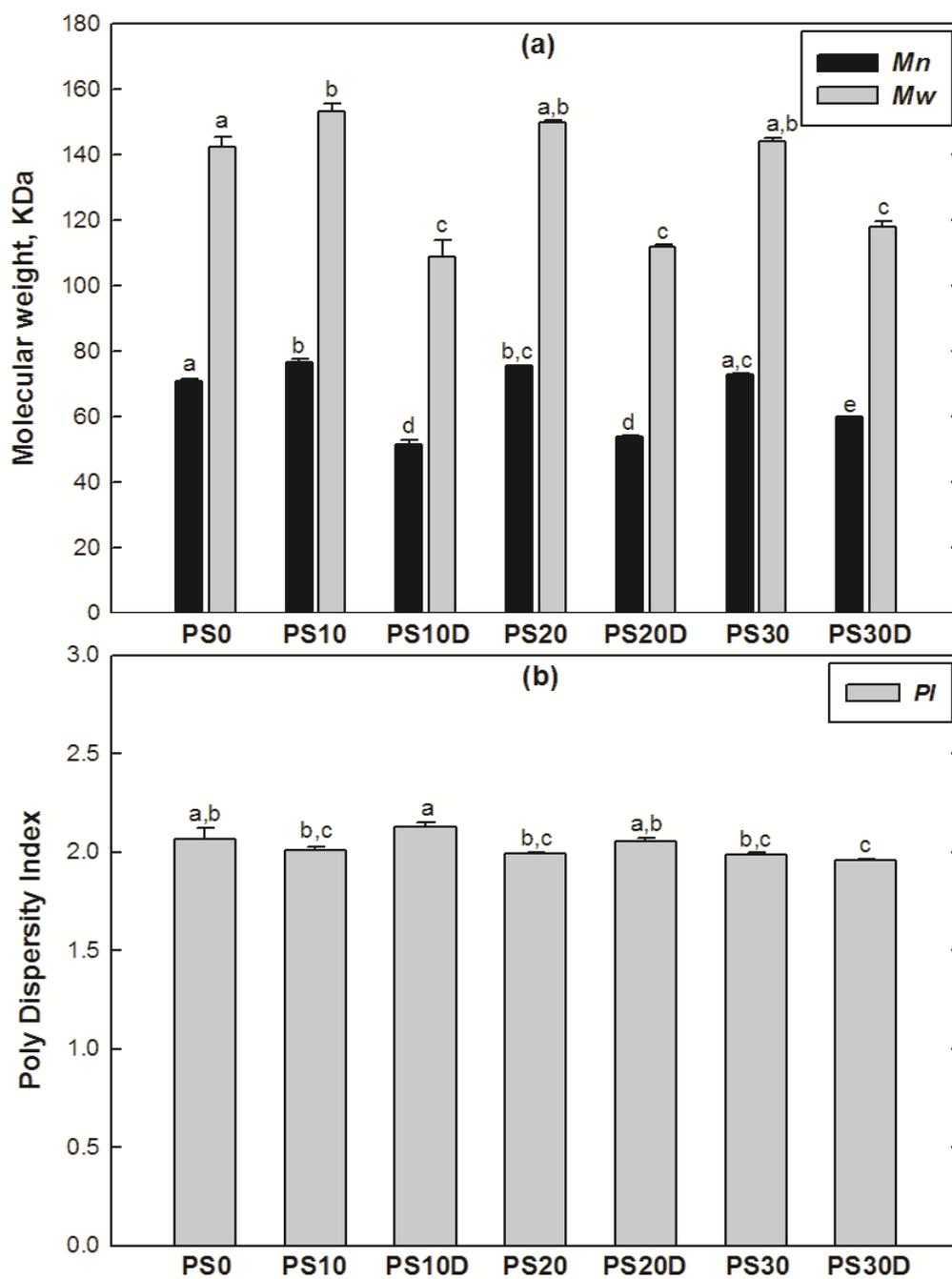


Figure 5.8 SEM micrographs of PLLA/starch blends after removing starch phase; magnified images ($\times 5,000$).

5.3.5 Molecular weight

Figure 5.9 a and b show the M_n , M_w , and PI of PLLA and PLLA/starch blends without and with reactive compatibilization. The effect of starch addition in PLLA seemed not to have much effect on molecular weight of neat PLLA; however, reactive compatibilization significantly decreased both M_n and M_w compared to PLLA/starch blends at the same starch concentration without compatibilization. The polydispersity index (PI) remained stable. This decrease of M_n and M_w could be attributed to the chain scission of PLLA chains induced by hydrolysis reactions in the PLLA/starch blends. Similar results were reported by Jang *et al.* where the molecular weight of MAH compatibilized blends decreased via chain scission of PLA molecules due to hydrolysis, back biting, and thermal degradation[41]. However, the reactive compatibilization in this study seemed not to have much effect on the thermal stability of PLLA/starch blends as seen in Figure 5.1 (b). This could be attributed to the chemical interaction between PLLA and starch by MAH improving thermal stability of the starch phase. Gao *et al.* reported that thermal stability of PLA/maleic anhydride grafted starch was slightly higher than those of other PLA/starch blends[42].



Bars with the same color followed by the same letter are not significantly different using Tukey's HSD adjustment t-test with type I error (α) of 0.05.

Figure 5.9 M_n , M_w (a) and PI (b) of PLLA/starch blends.

5.4 Conclusions

PLLA/starch blends were produced without and with MAH in the presence of DCP as initiator. MAH acted as a good compatibilizer for the PLLA and starch blends in the presence of DCP as an initiator. T_g and T_m decreased with reactive compatibilization; however, the thermo-mechanical properties of PLLA/starch with reactive compatibilization were significantly improved as compared blends with reactive compatibilization. A PLLA/starch (80/20) blend with 2.0 phr of MAH and 0.1 phr of DCP had an E' of 3.9 GPa at 40°C, and tensile strength of 51.7 MPa at 23°C, and elongation at break of 3.3 %, which were close to neat PLLA. Enhanced interfacial adhesion between PLLA and starch was observed due to the compatibilization effect of MAH grafted onto PLLA and starch. Reactive compatibilization significantly reduced combined molecular weight of PLLA/starch blends.

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CHAPTER VI

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CHAPTER VI

Dual Migration of α -Tocopherol and Resveratrol from Poly(L-lactic acid), PLLA, and PLLA/starch Blend Films into Ethanol

Abstract

Poly(L-lactic acid) (PLLA)/starch blends with various concentrations of two natural antioxidants, α -tocopherol (α -TOC) and resveratrol, were fabricated by a melt blending and compression molding process. The effects of the two antioxidants on the optical (color), thermal and mechanical properties of PLLA/starch blends with antioxidants were assessed. PLLA/starch blend films with α -TOC and resveratrol showed a yellowish color influenced by the combined effect of white starch and the brown color of the antioxidants. The glass transition and melting temperatures were significantly reduced with the addition of antioxidants while enhanced thermal stability was observed, which could be a benefit and important for processing and production. The enhanced mechanical properties could be attributed to not only a compatibilization effect based on the chemical linkage between PLLA and starch chain, but also restriction of the chain mobility by antioxidants. The release of resveratrol from PLLA and PLLA/starch blend films into ethanol followed Fickian behavior. The D values of α -TOC were found to be between $0.47 \sim 3.95 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA films and $0.70 \sim 6.83 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA/starch blend films at 13 °C, $5.67 \sim 13.0 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA films and $4.10 \sim 24.2 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA/starch blend films at 23 °C, and $89.0 \sim 118.0 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA films and $123 \sim 282 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA/starch blend films at 43 °C. The D values of resveratrol were found to be between $0.073 \sim 0.54 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA films and $1.42 \sim$

$6.93 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA/starch blend films at 13 °C, $0.90 \sim 3.44 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA films and $4.16 \sim 22.3 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA/starch blend films at 23 °C, and $24.8 \sim 74.1 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA films and $40.1 \sim 309 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA/starch blend films at 43 °C.

6.1 Introduction

Various petroleum based polymeric materials are widely used for food packaging materials, but resources are finite. The development of new types of polymers synthesized from natural renewable resources has been widely investigated, and poly(L-lactic acid) (PLA) is considered as one of the most promising polymers due to its biocompatibility and biodegradability under the specific composting conditions[1, 2]. The global lactic acid and PLA market is expected to grow by about US 3,800 million dollars by 2016[3]. PLA is currently used for single or multilayer films, trays, cups, and bottles, and can be manufactured by extrusion, thermoforming, injection and blow molding processes for packaging applications. It has been reported that PLA is also suitable for the production and use of functional membranes in various fields[1, 4, 5]. Although PLA shows good physical properties similar to polystyrene (PS) and polyethylene terephthalate (PET), the relatively higher oxygen permeability of PLLA and its brittleness are main drawbacks for flexible packaging application especially for foods and/or pharmaceuticals susceptible to oxidation.

Controlled release systems have been developed and are extensively being used in pharmaceutical, food and packaging applications[6]. Specifically, these have been used in drug delivery systems. Application of these systems to food packaging has increased since they enable

controlled release of active compounds such as antioxidants and antimicrobials from the packaging system at an appropriate rate during the storage of products, allowing protection and extension of the product's shelf life. One of the first applications of this technology was reported to extend the shelf life of oatmeal cereal packaged in high density polyethylene (HDPE) film added with a high concentration of butylated hydroxytoluene (BHT) added[7]. Wessling *et al.* studied the migration and sorption behavior of α -Tocopherol (α -TOC) and BHT in low density polyethylene (LDPE) in contact with a fatty food simulant, and found that the migration of α -TOC into the food simulant was slower than that of BHT[8]. Byun *et al.* prepared PLA antioxidant film with α -TOC, BHT, and polyethylene glycol 400 (PEG 400) by film casting technique. PLA film with BHT and PEG 400 (BP-PLA) had antioxidant activity due to the presence of BHT; however, it had less antioxidant activity when compared to PLA film with α -TOC, BHT and PEG 400 (ABP-PLA). The antioxidant activity of the ABP-PLA film was significantly increased by the addition of α -TOC into the BP-PLA film[9].

α -TOC is one of four tocopherols having antioxidant activity, and is the most abundant form in nature. It is a natural antioxidant present in grains like soybeans, cottonseed, and sunflowers. It has been widely known to be effective in preventing lipid peroxidation and other radical oxidative reactions[10, 11]. Min *et al.* reported that singlet oxygen oxidation produced undesirable compounds in foods during processing and storage, and carotenoids and tocopherols in foods can minimize singlet oxygen oxidation[12]. Wessling *et al.* reported that the addition of above 360 ppm of α -TOC in LDPE delayed the oxidation of linoleic acid at 6 °C. In addition, they also suggested possible change in the mechanical properties, color, and the oxygen permeability of LDPE film when α -TOC is added[13]. Manzanarez-López *et al.* reported that the diffusion of α -TOC from poly(L-lactic acid), PLLA films to ethanol simulant showed Fick's law

behavior with diffusion coefficients (D) at levels between $3.16 \pm 0.19 \times 10^{-11}$ and $5.29 \pm 0.71 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ at 23 and 33 °C, respectively. Diffusion to fractionated coconut oil was much lower than to ethanol. They also suggested the potential production of PLLA packages with added α -TOC for protection of oily foods[4]. Soto-Valdez *et al.*, from the same research group, also suggested that films produced with resveratrol could be used as antioxidant release membranes for a variety of pharmaceutical, medical, and food applications. Resveratrol is a polyphenolic compound, which is a natural antioxidant mainly present in grapes[14], grape juice[15], wine[16], peanuts[17], and a number of other plant species[18]. Resveratrol has relatively good thermal stability with a melting temperature of around 255 °C. The two aromatic rings in resveratrol showed a higher radical-scavenging capacity than propyl gallate, ascorbic acid and α -TOC (see Figure 1)[19]. Mielink *et al.* found that the oxygen scavenging efficiency of grape seed extracts increased with increasing antioxidant concentration from 0.4 to 1.6 $\text{g} \cdot \text{kg}^{-1}$, suggesting potential application of resveratrol to active packaging[20]. Soto-Valdez *et al.* recently prepared PLLA films containing 1 and 3 wt.-% resveratrol, and found that the diffusion of resveratrol from PLLA film into ethanol showed Fickian behavior. The D values were found to be between $3.47 \pm 0.10 \times 10^{-13}$ and $8.51 \pm 0.38 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ between 9 and 43 °C[5].

Many researchers have evaluated the release of antioxidant compounds from homopolymers such as LDPE, HDPE and polypropylene (PP) to improve shelf life of food product[7, 13]. However, little research has been directed towards evaluating the dual release of antioxidants from polymer blends, which may allow a more complex and targeted release of antioxidants. The design of these functional membranes can create new opportunities for extending food products' shelf life and the creation of new pharmaceutical applications.

Thus, the overall goal of this work was to develop a PLLA/starch blend film containing two natural antioxidants, α -TOC and resveratrol, for creating new functional membranes. In a previous series of papers, we have presented the properties of PLLA films with added α -TOC and resveratrol and developed a PLLA starch blend grafted with maleic anhydride (MAH)[21-23]. In the work presented in this paper, the effect of adding both antioxidants on the PLLA/starch blend films on optical, thermal, and thermo-mechanical properties were assessed. Specifically, the simultaneously release kinetics of α -TOC and resveratrol from PLLA/starch blend films to ethanol was evaluated. Values were compared with the release kinetics of α -TOC and resveratrol from PLLA films.

6.2 Experimental

6.2.1. Materials

Poly(94% L-lactic acid), PLLA (4042D), resin was provided by NatureWorks LLC, Minnetonka, MN. α -TOC (97+ % purity) and resveratrol (99% purity) were purchased from Alfa Aesar (Ward Hill, MA, USA) and ChromaDex Inc. (Santa Ana, CA, USA), respectively. The chemical structures of both antioxidants are given in Figure 6.1. Dicumyl peroxide (DCP) and MAH (briquettes, 99%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). PLLA was dried in a vacuum oven at 60 °C for 24 h, and starch was dried in a vacuum oven at 120 °C for 3 h in order to remove residual moisture. All solvents used for quantification were HPLC grade, and obtained from Sigma-Aldrich (St. Louis, MO, USA).

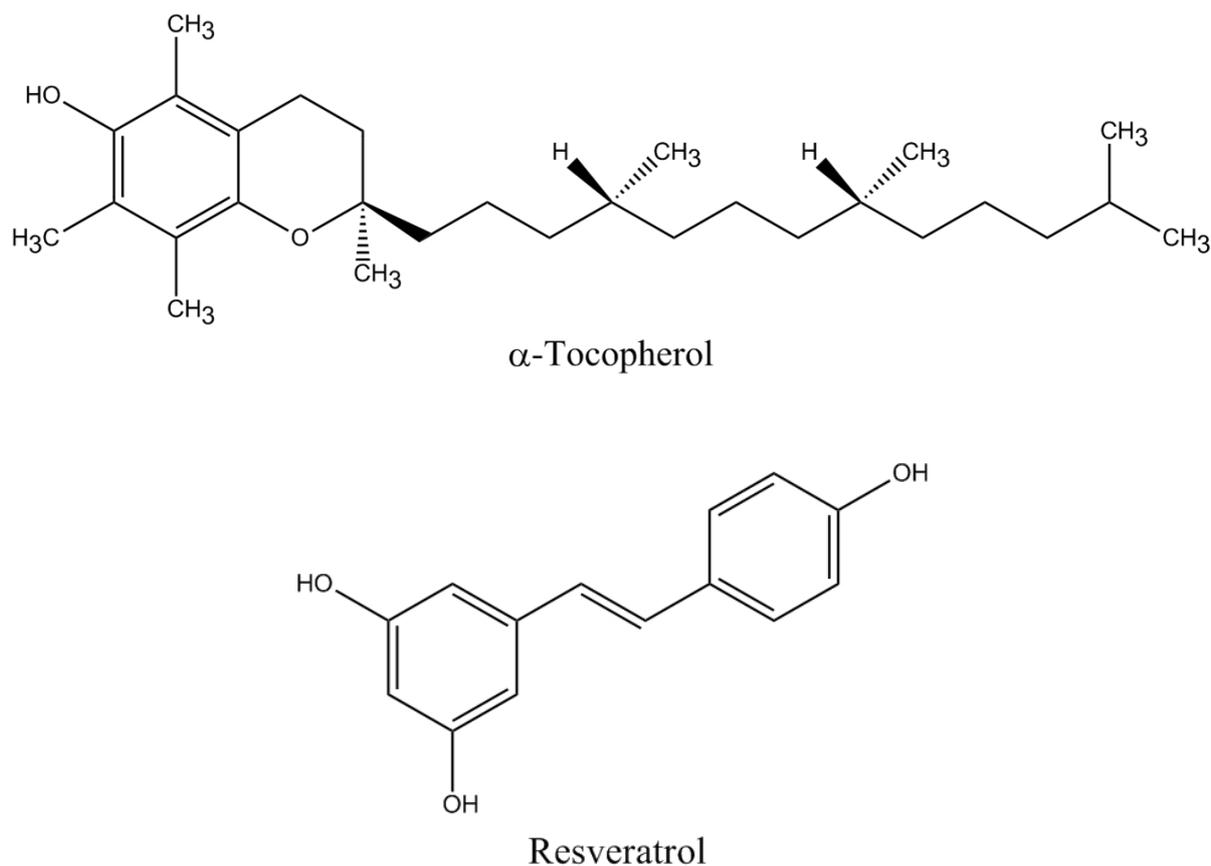


Figure 6.1 Chemical structures of α -Tocopherol (α -TOC) and Resveratrol

6.2.2 Preparation of PLLA/starch blends with antioxidants

PLLA/starch blends with various concentrations of both α -TOC and resveratrol were prepared in an intermixer, Brabender Plasticoder, PLE 331 (Brabender, Duisburg, Germany) at 190°C with a rotor speed of 60 rpm, and the total mixing time was fixed at 12 min. An 80/20 (weight percent, wt%) of PLLA/starch blend ratio was used in this study, and 0.1 phr of DCP and 2 phr of MAH were fixed for compatibilization of PLLA and starch. It was previously demonstrated that this blend provides the best film properties[22]. The nominal composition and nomenclature of the films produced with the two antioxidants are provided in Table 6.1. The PLLA/antioxidants mixtures were cooled to room temperature and then compression molded to a film with a

thickness of 220 ~ 270 μm by a hydraulic laboratory press model 3925 (Carver, Wabash, IN) at 200 $^{\circ}\text{C}$. All samples were kept at refrigeration conditions (-15 $^{\circ}\text{C}$) to prevent possible migration of antioxidants from the films. PLLA films with the same composition of antioxidants were previously prepared. Details of the preparation technique for these films and their properties can be found elsewhere[21].

6.2.3 Characterization

6.2.3.1 Optical properties

The total color difference (ΔE^*) of PLLA/starch blend films with two antioxidants were determined as described by the Commission Internationale de l'Eclairage (CIE) $L^*a^*b^*$ color scale with a spectro-colorimeter (JS555, Color Techno System Corporation, Tokyo, Japan).

6.2.3.2 Thermal properties

The glass transition temperature (T_g), melting temperature (T_m), and percent crystallinity (X_c) were obtained with a differential scanning calorimeter (DSC) (DiamondTM DSC, Perkin-Elmer, Waltham, MA, USA). The measurements were carried out under nitrogen atmosphere with a temperature range from 20 to 220 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$, and were analyzed by Diamond Analysis software. The percent crystallinity was determined by Eq. (1)[24].

$$x_c(\%) = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^c (1 - x)} \times 100 \quad (1)$$

where ΔH_m is enthalpy of fusion, ΔH_c is the enthalpy of cold crystallization, ΔH_m^c is enthalpy of fusion of pure crystalline PLA ($\Delta H_m^c = 93.1 \text{ J}\cdot\text{g}^{-1}$ [24]), and x is the sum of fractions of antioxidants and starch.

A thermo-gravimetric analyzer (TGA Q600, TA instruments, New Castle, DE) was used to measure the change of sample weight. The analysis was performed up to 800 °C with a rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ under a nitrogen atmosphere with a flow rate of 20 sccm.

6.2.3.3 Thermo mechanical properties

Dynamic mechanical analysis (DMA) of the PLLA/starch blends with antioxidants was performed on a Perkin–Elmer dynamic mechanical analyzer, N535. Samples with a width of 6.0 – 6.5 mm and a length of 8 – 10 mm were cut for testing in tension mode. The sample dimensions were carefully measured and the mean values of 5 measurements of the samples were inserted into the instrument. The experiments were carried out at a heating rate of $3 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ and a temperature range of $-20 \sim 170 \text{ }^\circ\text{C}$ with a frequency of 1 Hz. The storage modulus (G') and loss tangent ($\tan \delta$) were measured for each blend sample in this temperature range.

6.2.3.4 Mechanical properties

Tensile strength, Young's modulus, and elongation at break were assessed by a Universal Test Machine (UTM) (Instron 4465, Instron, Canton, MA) according to ASTM D 882-02. Samples were cut into strips with dimensions of $1 \times 8 \text{ cm}$ and conditioned at $23 \text{ }^\circ\text{C}$ and 50 % RH for 24 h

before testing. The specimens were tested at a crosshead speed of $10 \text{ mm} \cdot \text{min}^{-1}$ with a 4 cm initial gap separation.

6.2.3.5 Molecular weight measurement

The combined molecular weight of the PLLA/starch blends without and with antioxidants was determined with a gel permeation chromatograph (GPC) (Alliance GPCV 2000 system, Waters, Milford, MA, US). Sample films (20 mg) were dissolved in 10 ml of chloroform (CHCl_3) (Merck, Darmstadt, Germany), and then 100 μl of each sample solution were injected into the GPC. The GPC was equipped with an isocratic pump, an autosampler, a series of 2 columns (Waters Styragel[®] HR5E and HR4E), and a refractive index detector. A flow rate of $1 \text{ ml} \cdot \text{min}^{-1}$, a runtime of 40 min, and a temperature of $35 \text{ }^\circ\text{C}$ were used. The Mark-Houwink corrected constant $K = 0.0131 \text{ (mL} \cdot \text{g}^{-1})$ and $a = 0.759$ for dilute PLLA solution in chloroform at 30°C determined by Dorgan and coworkers were used[25].

6.2.3.6 Quantification of α -TOC and resveratrol after processing film

To determine the actual concentration of α -TOC and resveratrol after processing, the compounds were extracted from PLLA and PLLA/starch blend films with antioxidants (0.25 cm^2 pieces) in methanol at $40 \text{ }^\circ\text{C}$ for 24 h in dark conditions. Butylated hydroxytoluene (BHT) ($100 \mu\text{g/mL}$) was introduced to protect the antioxidants from degradation during the extraction period. Quantification was performed with an ultra-performance liquid chromatograph (UPLC) (Waters ACQUITY UPLC, Milford, USA) equipped with a PDA detector. An ACQUITY BEH C_{18}

column (50 × 2.1 mm) (Waters) with an isocratic elution of methanol:water (98:02) at a flow rate of 0.15 mL/min and 5 µL of injection volume were used. Calibration curves were generated by using solutions with both α-TOC and resveratrol in methanol (0.50 to 50 µg/mL), and triplicates for both standard solutions were performed. ($R^2 = 0.9997$ for α-TOC, $R^2 = 0.9993$ for resveratrol)

6.2.3.7 Diffusion of α-TOC and resveratrol from PLLA and PLLA/starch blend film

Diffusion of antioxidants from the PLLA and PLLA/starch blend films without and with antioxidants to 100% ethanol (a food simulant) was performed using a migration cell in accordance with ASTM D4754-98 (2003). Ethanol was used as an alcoholic food simulant. The test cells consisted of 40 ml glass amber vials with screw tops with hole caps and PTFE/silicon sealing septum[26]. Round test specimens (approximately diameter 18 mm) were cut from the PLLA and PLLA/starch films, and were immersed in 30 mL of ethanol. Specimens were separated by means of glass beads to avoid contact between films. (Figure 6.2) The vials were stored at three different temperatures (13, 23, and 43 °C) for a period of time long enough to determine the release of the antioxidants. Simulant samples were taken periodically during 24 and/or 48 hr for quantification.

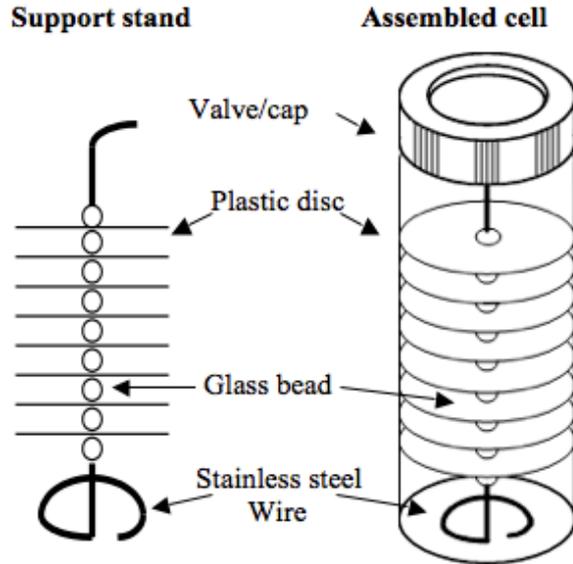


Figure 6.2 The two-sided liquid extraction technique for sample discs using an FDA migration cell. Adapted from ASTM D 4754-98 (2003)

The one dimensional diffusion solution equation of Fick's second law for the two antioxidants, α -TOC and resveratrol, from the films to a limited volume solution was used to determine the diffusion coefficient (D) (2) and (5)[27]:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} \exp\{-Dq_n^2 t / l^2\} \quad (2)$$

where l is thickness of the plastic film

q_n are the non zero positive roots of $\tan q_n = -\alpha q_n$, and α is expressed as

$$\alpha = \frac{V_S}{V_P \cdot K_{P,S}} \quad (3)$$

where V_S and V_P are molar volume of simulant and the plastic film or package

$K_{P,S}$ is the partition coefficient of α -TOC and resveratrol between plastic film and the simulant

The partition coefficient could be calculated from the ratio of the concentration of α -TOC and resveratrol in PLLA and PLLA/starch blends ($C_{P,\infty}$) and the simulant ($C_{S,\infty}$) at equilibrium according to the following Equation (4)

$$K_{P,S} = \frac{C_{P,\infty}}{C_{S,\infty}} \quad (4)$$

The Fick's second diffusion relationship (5) shown below was applied to determine the diffusion coefficient (D) when the amount of solvent can be considered very large and $\alpha \gg 1$ since $V_S \gg V_P$ and/or $K_{P,S} < 1$, so Equation (2) can be simplified as:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp\left\{-D(2m+1)^2 \pi^2 t / l^2\right\} \quad (5)$$

where l is thickness of the plastic film

The mass of antioxidants diffused at time t , divided by the mass of antioxidants diffused at equilibrium (M_t/M_∞) were plotted as function of the square root of time t ($\text{sec}^{1/2}$) and the diffusion coefficients (D) were determined at each different temperature.

To determine the fit of the experimental data to Equations (2) and (5), the non-linear regression function in MATLAB[®] R2010a (MathWorks, Natick, MA, USA) was applied to the data[4, 28-31].

6.2.3.8 Activation energy determination

To assess the effect of temperature on the diffusion behavior of α -TOC and resveratrol from PLLA and PLLA/starch blend films without and with antioxidants into ethanol, the activation energy (E_a) was determined using the Arrhenius equation for diffusion (6):

$$D = D_0 \exp[-E_a / RT] \quad (6)$$

D : diffusion coefficient

D_0 : pre-exponential factor of diffusion

E_a : activation energy

R : gas constant, 8.3145 J / mol

T : temperature, K

E_a was obtained from the slope of a plot of reciprocal of temperature ($1/T$) versus the logarithm of D . ($E_a = -\text{slope} \times 2.303 R$)

6.2.3.9 Statistical Analysis

Statistical analyses of the results from the PLLA/starch blends without and with antioxidants were performed with SPSS software (SPSS, Inc., Chicago, IL). One-way analysis of variance using the General Linear Model procedure and Tukey's honestly significant difference (HSD) tests were used to determine significant differences ($\alpha < 0.05$).

6.3 Results and discussion

We previously manufactured PLLA with two antioxidants; α -TOC and resveratrol to evaluate the performance of the PLLA film when two antioxidants were added to the film and to convert the

PLLA film into a functional membrane for sustained release of antioxidants. The optical, physical, thermal and mechanical properties of PLLA films were assessed when a range of different concentrations of α -TOC and resveratrol was added to the film[21].

The addition of α -TOC and resveratrol increased the a^* (redness) and b^* (yellowness) values of the PLLA/antioxidant films. These samples showed slightly more hydrophobic characteristics than neat PLLA due to the increase of the dispersive component from surface free energy. Enhancement of the elastic modulus with varying concentrations of the two antioxidants was found in PLLA/antioxidant films. It was also confirmed that the combinations of α -TOC and resveratrol have a critical role on percent transmission ($\%T$), glass transition temperature (T_g) and percent crystallinity (X_c). Both antioxidants affected the mechanical and thermo-mechanical properties of PLLA films, suggesting that further investigation of the effect of the antioxidants on mechanical properties would be needed. The melt viscosity of the PLLA/antioxidant films was substantially higher than that of neat PLLA. The dynamic storage modulus, $G'(\omega)$ of the PLLA/antioxidant films was found to be higher than that of neat PLLA film over the entire frequency range. These higher melt viscosity and $G'(\omega)$ values could be an indication of formation of entanglements between the PLLA and α -TOC and resveratrol. These results show potential feasibility for using PLLA/antioxidant films as active functional membranes for food, pharmaceutical, and medical packaging applications.

The total amount of antioxidants in the PLLA and PLLA/starch films after processing is shown in Table 6.1. Around 72.9 ~ 81.5 % of total initial antioxidant remained in the five PLLA films, and around 73.5 ~ 96.4 % of both antioxidants remained in the five PLLA/starch blends after processing. Soto-Valdez *et al.* reported the loss of resveratrol from PLA films with 1 ~ 3 %

of resveratrol was 16.7 and 25.5 %, and Manzanarez-Lopez *et al.* also found 15.7 % loss of α -TOC from 3% of α -TOC added PLLA films. As reported, the loss of α -TOC and resveratrol could be attributed to thermal degradation during mixing process in this study.

Table 6.1 Nominal and after processing composition of antioxidants in the PLLA and PLLA/starch blends films

Sample	Nominal		After Processing			
	α -TOC (mg/g resin)	Resveratrol (mg/g resin)	PLLA		PLLA/starch	
			α -TOC (mg/g resin)	Resveratrol (mg/g resin)	α -TOC (mg/g resin)	Resveratrol (mg/g resin)
T0R5	0	50	n/a	n/a	n/a	48.2 \pm 0.3
T1R4	10	40	7.8 \pm 0.2	33.0 \pm 0.8	7.6 \pm 0.2	35.6 \pm 0.1
T2R3	20	30	13.2 \pm 0.1	25.4 \pm 0.5	N/A	n/a
T2R2	25	25	14.8 \pm 0.2	19.9 \pm 0.1	19.7 \pm 0.7	23.1 \pm 0.5
T3R2	30	20	20.8 \pm 0.5	18.1 \pm 0.5	n/a	n/a
T4R1	40	10	29.6 \pm 0.9	6.9 \pm 0.1	22.8 \pm 0.4	9.1 \pm 0.1
T5R0	50	0	n/a	n/a	36.7 \pm 1.7	n/a

n/a: Not Available

It is interesting to note that a higher amount of resveratrol remained in both PLLA and PLLA/starch blend films after processing than did α -TOC. This could be related to the better thermal stability of resveratrol than that of α -TOC. Resveratrol is known to have relatively good thermal stability with a melting temperature of 267 °C[32].

6.3.1. Optical properties

PLLA/starch blends without and with antioxidants displayed a yellowish color with various intensities as shown Figure 3. The PLLA/starch blend film without antioxidant (T0R0) was used

as a reference film. The addition of the two antioxidants significantly affected the lightness (L^*) and yellow (b^*) color of the PLLA/starch blend films while minor differences in the green (a^*) color of the blend films were observed. The total color difference (ΔE) of the blend films was between 16.5 ~ 25.4 indicating that the addition of α -TOC and resveratrol had a great effect on color difference, and this color difference was perceptible to the naked eye, and T0R5 shows significant difference from T5R0. But difference among other antioxidant added film could not be differentiated. (Figure 6.3)

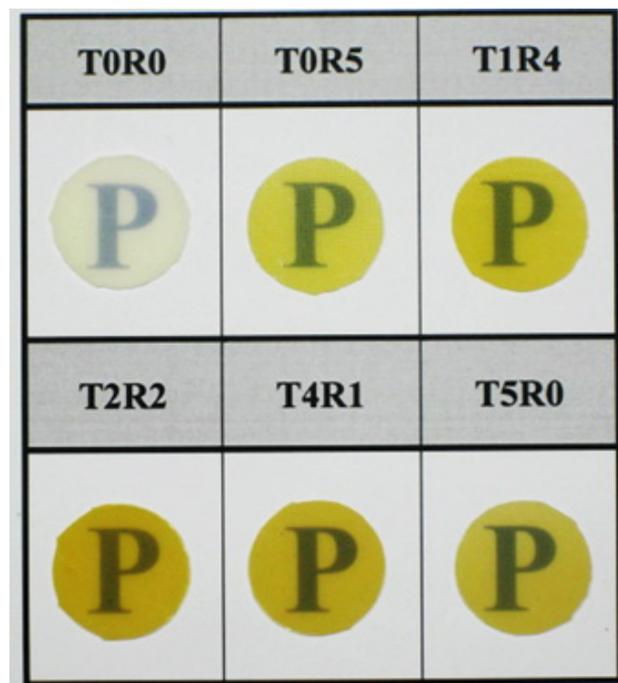


Figure 6.3 The appearance of PLLA/starch blends without and with antioxidants

In the case of PLLA films with added these two antioxidants, there was a significant difference between neat PLLA and PLLA films with antioxidants as well due to the nature of α -TOC

having a clear yellowish brown color and resveratrol having a dark brown color indicated by the higher a^* (redness) and b^* (yellowness) values[26].

Table 6.2 L^* , a^* , b^* and ΔE^* of PLLA/starch blend films added with α -TOC and resveratrol

Sample	L^*	a^*	b^*	ΔE^*
T0R0	55.3 ^a	-1.3 ^a	3.6 ^a	-
T0R5	49.5 ± 0.9 ^b	-4.3 ± 0.1 ^b	19.4 ± 0.9 ^b	17.0 ± 0.6 ^a
T1R4	48.9 ± 0.7 ^b	-3.7 ± 0.0 ^b	24.3 ± 1.8 ^{cd}	21.8 ± 1.0 ^b
T2R2	50.2 ± 0.8 ^b	-1.5 ± 0.2 ^a	28.5 ± 0.6 ^d	25.4 ± 0.4 ^c
T4R1	49.8 ± 0.4 ^b	-1.3 ± 0.0 ^a	22.0 ± 0.2 ^{bcd}	19.1 ± 0.2 ^d
T5R0	49.6 ± 0.8 ^b	-1.6 ± 0.1 ^a	19.1 ± 0.7 ^{bc}	16.5 ± 0.4 ^a

Values in the same column with different superscript letters are significantly different at $\alpha = 0.05$; All of the values are expressed as average values ± standard error:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

$$\Delta L^* = L_{sample}^* - L_{standard}^*$$

$$\Delta a^* = a_{sample}^* - a_{standard}^*$$

$$\Delta b^* = b_{sample}^* - b_{standard}^*$$

The standard value is the initial value for PLLA/starch film

6.3.2. Thermal properties

The results of the thermal analysis for PLLA/starch blends without and with antioxidants are presented in Table 6.3 and Figure 6.4. The addition of two antioxidants to PLLA/starch blends significantly decreases T_g and T_m . This could be due to the plasticizing effect of the antioxidants on PLLA/starch blends. In our previous work, 3 to 5 °C reduction of T_g and T_m was found at PLLA/antioxidants film with similar concentration of α -TOC and resveratrol[21]. Similar results

were recently reported by Soto *et al.* when adding resveratrol[5]. The addition of 1 ~ 3% of resveratrol also decreased T_m of PLA film (about 1 °C). Manzanarez *et al.* also found a small reduction of T_g and T_m with addition of α -TOC in PLA film (about 1 °C)[4]. In this study, T_g and T_m were reduced about 2 to 6 °C, and this could be due to higher concentration of both antioxidant resulting in much greater plasticization effect. As seen in Figure 4, the addition of two antioxidants broadened the T_{cc} peak of PLLA/starch blends indicating that the crystal growth of the PLLA chain was hindered by antioxidants. This is confirmed by the significant decrease of X_c for the PLLA/starch blends with antioxidants.

Table 6.3 Thermal properties and % crystallinity of PLLA/starch blend films without and with antioxidants

Sample	T_g , °C	T_m , °C	X_c , %
T0R0	53.1 ± 0.0 ^a	153.5 ± 0.2 ^a	3.1 ± 0.0 ^a
T0R5	51.6 ± 0.4 ^b	148.0 ± 0.2 ^b	2.4 ± 0.5 ^{ab}
T1R4	49.8 ± 0.1 ^c	147.5 ± 0.2 ^b	2.5 ± 0.1 ^{ab}
T2R2	49.0 ± 0.1 ^d	149.8 ± 0.1 ^c	2.3 ± 0.5 ^b
T4R1	48.4 ± 0.4 ^e	150.2 ± 0.4 ^{cd}	2.2 ± 0.3 ^b
T5R0	47.4 ± 0.0 ^f	150.4 ± 0.2 ^d	2.1 ± 0.4 ^b

Values in the same column with different superscript letters were significantly different at $\alpha = 0.05$; All of the values are expressed as average values and standard error.

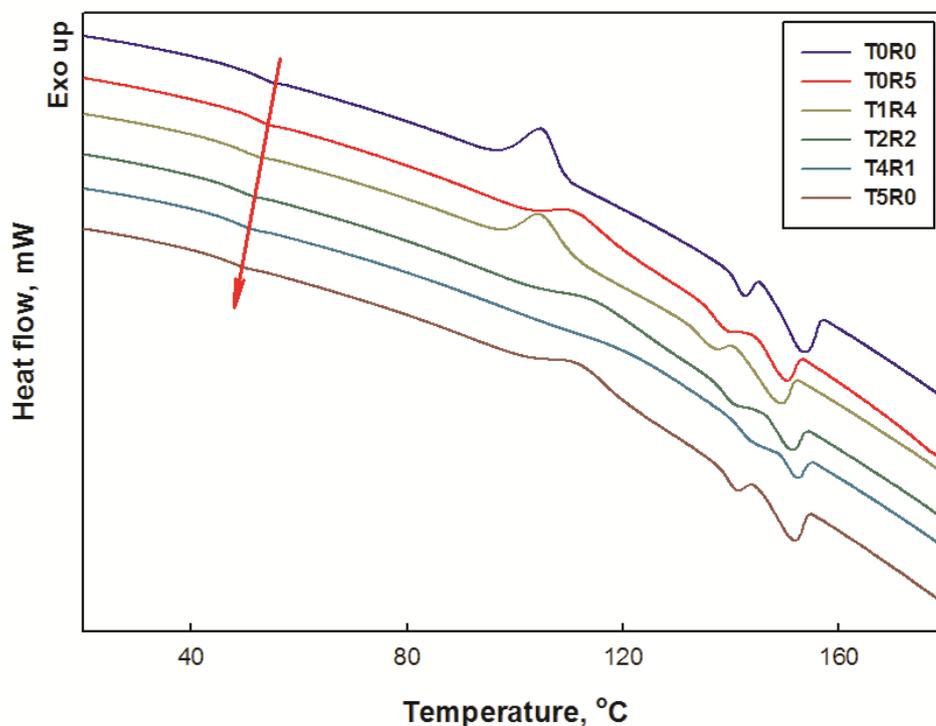


Figure 6.4 DSC thermogram of PLLA/starch without and with antioxidants

Figure 6.5 shows the thermal stability of the PLLA/starch blends without and with antioxidants. T0R5 displayed the highest thermal stability with an onset degradation temperature of 265 ~ 267 °C. The onset decomposition temperature decreased as the α -TOC content increased. Arora *et al.* reported that α -TOC is thermally stable up to a temperature of about 240 °C; thereafter, it undergoes a sharp mass loss, losing about 95% of its original mass at around 460 °C[33]. T5R0 showed a similar thermogram pattern. However, it can be seen that the addition of both antioxidants can have a significant effect on the thermal stability of PLLA/starch blends, providing additional benefit for industrial production applications. Enhanced thermal stability due to the addition of resveratrol was also found in PLLA film with antioxidants in our previous study[21].

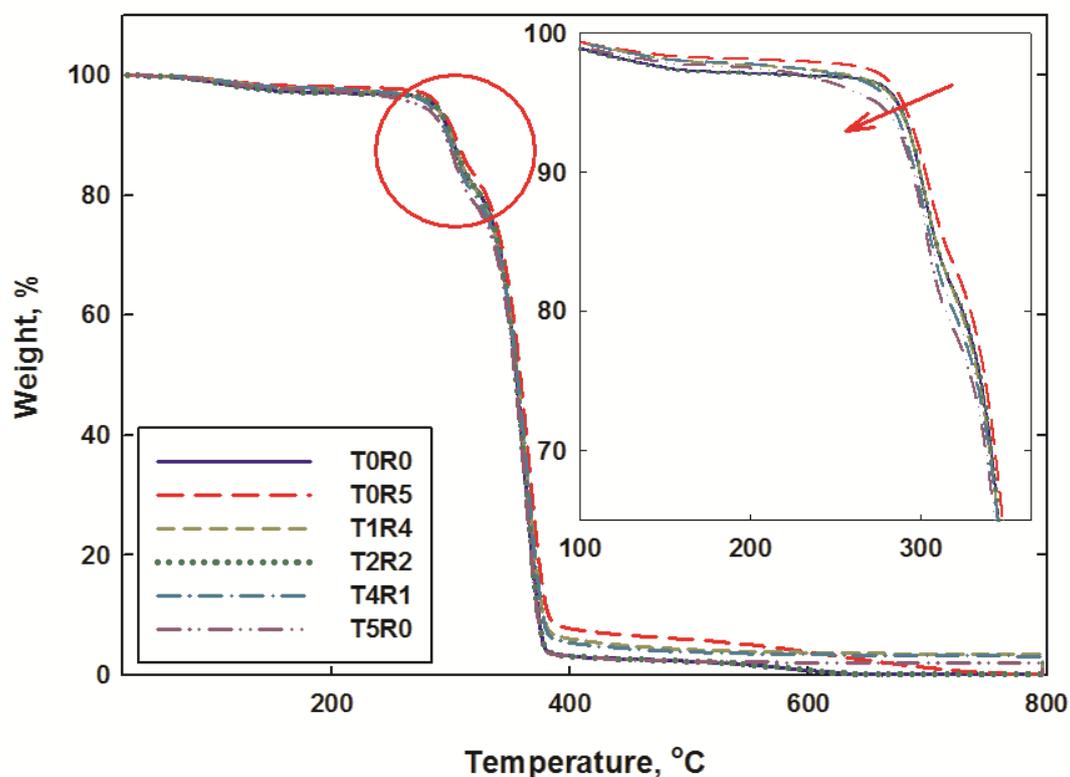


Figure 6.5 TGA thermogram of PLLA/starch without and with antioxidants

6.3.3. Thermo mechanical properties

Figure 6.6 a and b show the storage modulus (G') and loss modulus (G'') of the PLLA/starch blends without and with antioxidants. The onset temperature in the transition region decreased as α -TOC content increased due to plasticization. The blends with only resveratrol showed slight higher onset temperature, indicating the resveratrol did not have a critical role in changing T_g . In addition, the recrystallization temperature increased with addition of antioxidants. T5R0 had the lowest recrystallization temperature, indicating that addition of α -TOC induced slightly faster crystal growth, while the molecular hindrance from resveratrol resulted in slower crystal growth. In the PLLA film with antioxidants, elasticity also increased with a higher concentration of

resveratrol, while a larger plasticizing effect was observed for samples with higher concentration of α -TOC[21].

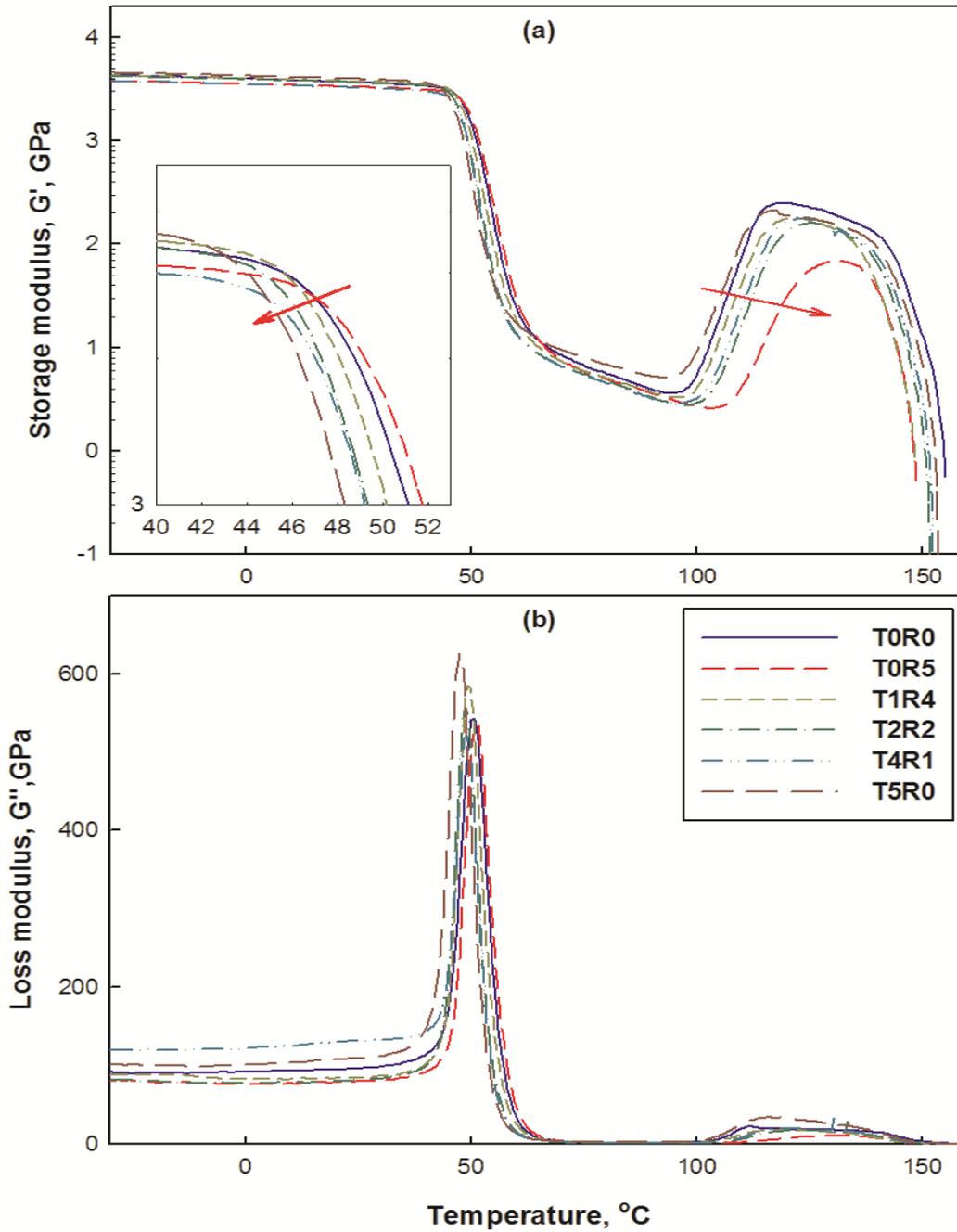


Figure 6.6 DMA thermogram of G' and G'' (b) of PLLA/starch blends without and with antioxidants

The damping factor, $\tan \delta$, is presented in Figure 6.7, and appears to be little affected by the addition of the two antioxidants. T0R5 showed better damping ability in the temperature range of 100 ~ 120 °C compared to other samples, due to better thermal stability.

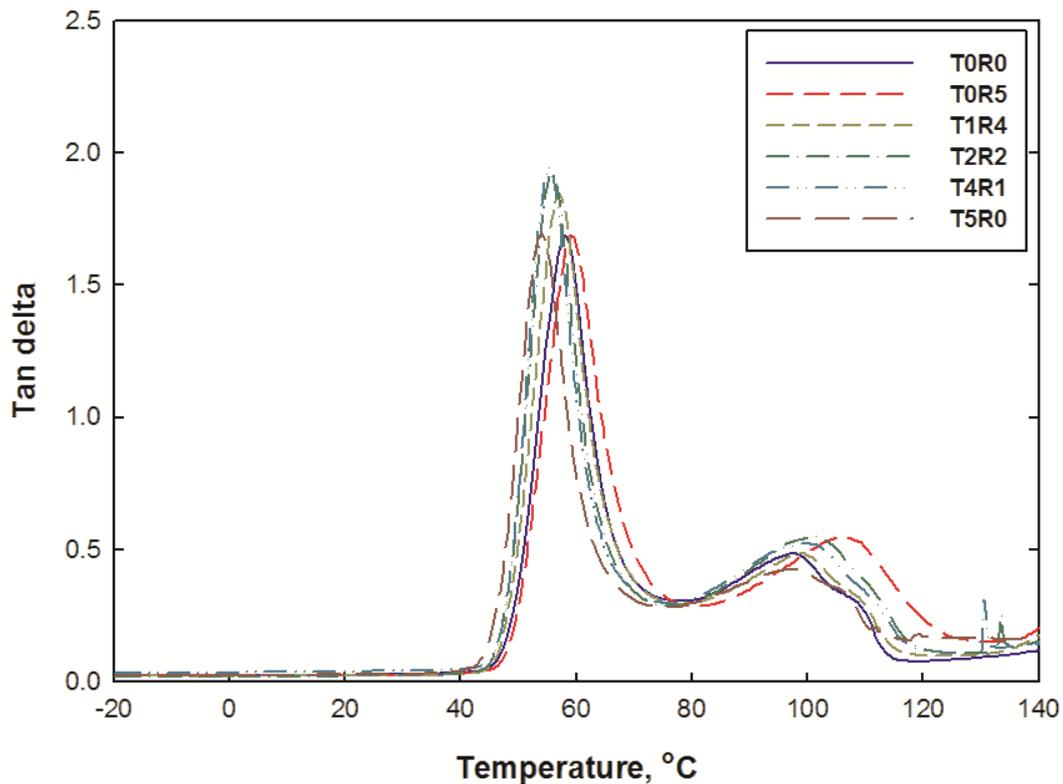


Figure 6.7 $\tan \delta$ of PLLA/starch blends without and with antioxidants

6.3.4. Mechanical properties

The effects of both antioxidants on the tensile strength, Young's modulus, and elongation at break of PLLA/starch blends without and with antioxidants are shown in Table 6.4. The tensile strength and modulus significantly increased with the addition of the two antioxidants. This could be attributed to not only the compatibilization effect based on the chemical linkage between PLLA and starch chains, but also to the restriction of chain mobility by the antioxidants.

Elongation at break was also slightly increased as compared to PLLA/starch blends without antioxidants. PLLA films with both antioxidants also showed increased tensile strength and modulus, except for film with a high concentration of α -TOC. The amount of α -TOC beyond some critical point may weaken intermolecular forces between adjacent PLLA chains and cause disentanglement, resulting in poor mechanical properties in films with higher concentrations of α -TOC[21].

Table 6.4 Mechanical Properties of PLLA/starch blends without and with antioxidants

Sample	Tensile strength, MPa	Modulus, GPa	Elongation at break, %
T0R0	34.2 ± 1.9^a	2.3 ± 0.1^a	1.8 ± 0.3^a
T0R5	48.2 ± 1.1^b	2.3 ± 0.1^{ab}	2.3 ± 0.2^b
T1R4	47.7 ± 5.9^b	2.6 ± 0.3^{ab}	2.2 ± 0.4^{ab}
T2R2	51.5 ± 3.7^b	2.5 ± 0.1^{ab}	2.4 ± 0.0^b
T4R1	48.2 ± 3.3^b	2.4 ± 0.2^{ab}	2.2 ± 0.2^{ab}
T5R0	49.3 ± 3.4^b	2.6 ± 0.0^b	2.1 ± 0.2^{ab}

Values in the same column with different superscript letters were significantly different at $\alpha = 0.05$; All of the values are expressed as average values and standard error.

6.3.5. Molecular weight measurement

Molecular weights of PLLA/starch blend films without and with antioxidants before migration are given in Figure 6.8. No significant change was found for samples added with resveratrol and α -TOC. Jang *et al.* reported that extruded PLA/starch blends at the ratio of 50:50 and 70:30, showed decrease of M_w and broadening of PI, and this was attributed to existing moisture in starch, leading to hydrolysis reaction of PLA[34]. In addition, reactive compatibilization of MAH onto PLLA and starch in PLLA/starch blends showed a significant effect on decreasing

both M_n and M_w due to the PLLA chain scission induced by hydrolysis of the PLLA/starch blends, as previously shown by Hwang *et al.*[23]. In this study, no significant decrease in molecular weight was found, and it appears that the addition of the two antioxidants reduced chain scission of the PLLA in the PLLA/starch blends. This is also consistent with the positive effect of the antioxidants on the thermal stability of the films.

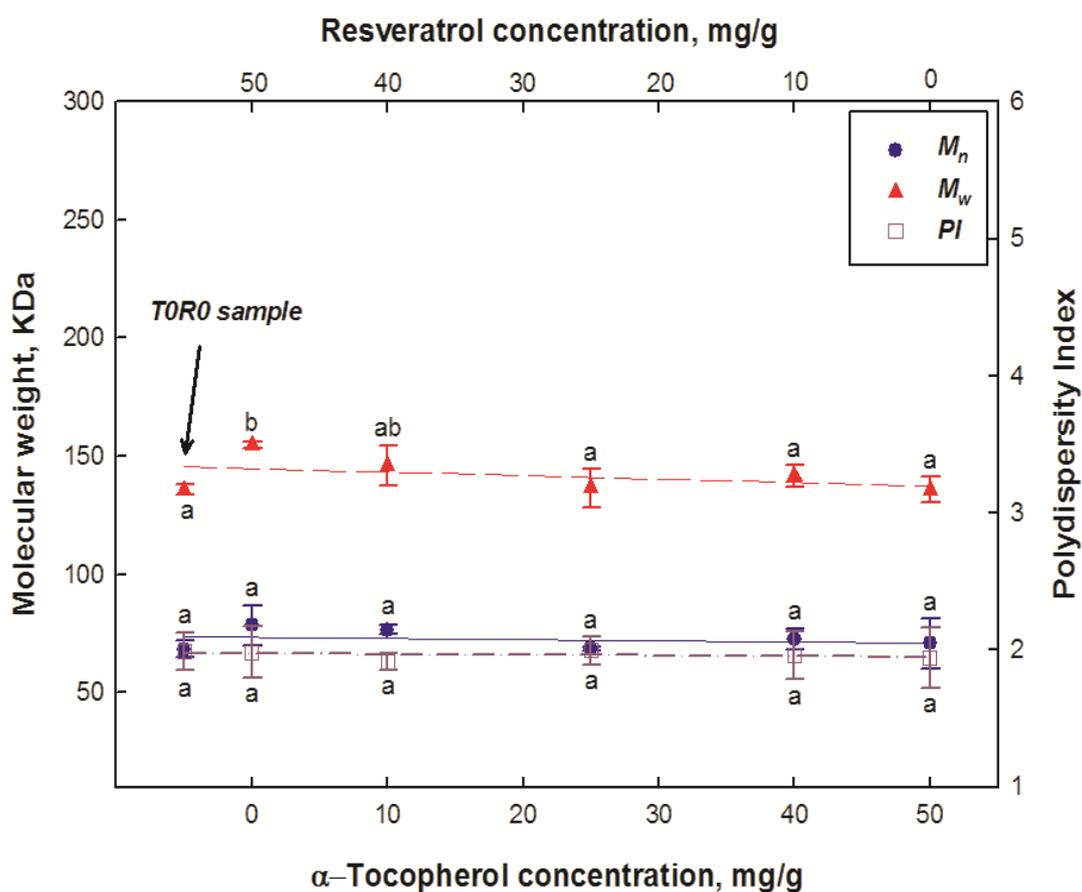


Figure 6.8 Number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PI) of PLLA/starch blends without and with two antioxidants

6.3.6. Partition coefficients of α -TOC and resveratrol from PLLA and PLLA/starch blend films

Tables 6.5 and 6.6 show the partition coefficients ($K_{p,s}$) and α value of α -TOC and resveratrol as indicated by Eq (4) and Eq (3), respectively, for the PLLA and PLLA/starch films. The partition coefficient indicates the relative solubility of the migrants, α -TOC and resveratrol, between the polymers and ethanol at equilibrium. $K_{p,s} > 1$ expresses a higher concentration of α -TOC or resveratrol in the PLLA or PLLA/starch blend film compared to that in ethanol. As seen in Table 5 and 6, the $K_{p,s}$ values for both α -TOC and resveratrol for 43 °C were found to be the lowest having the faster migration behavior from all PLLA and PLLA/starch blend films, indicating that the antioxidant concentrations in ethanol were much higher than in the films. It is interesting that the $K_{p,s}$ values of PLLA/starch blend films for α -TOC or resveratrol showed lower values at all three temperature as compared to PLLA films. It could be assumed that the amount of both antioxidants dispersed in starch would be higher than that of PLLA since the molecular interaction between antioxidants and starch would be greater than that of PLLA due to the larger number of hydroxyl groups. Therefore, the antioxidants in starch phase would be expected to have faster migration than PLLA resulting in lower $K_{p,s}$ values in PLLA/starch blend system. In addition, resveratrol showed the lower $K_{p,s}$ value indicating α -TOC has larger final concentration in the PLLA and PLLA/starch blends. Soto-Valdez *et al.* reported the $K_{p,s}$ values of 1143.1 and 506.1 for PLLA film with 1 and 3 wt% of resveratrol at 9 °C, and lowest values were found at 43 °C[5]. $K_{p,s}$ values of 796.6, 115.2, and 2.69 at 23, 33, and 43 °C were calculated from the study of PLLA with 2.58 wt% of α -TOC[4]. In this study, the $K_{p,s}$ values for each antioxidants

were found to be much lower at low temperature and vice versa. The PLLA and PLLA/starch blend films with two antioxidants were prepared by compression molding process, and the molded films have much thicker than sample films produced by blow-extrusion process[4, 5, 31]. Therefore, the migration behavior of both antioxidants in films having different morphology are different from other studies resulting in different $K_{p,s}$ values. Further investigation would be required.

Table 6.5 Partition Coefficient ($K_{p,s}$) of α -TOC from PLLA and PLLA/starch blend films into Ethanol at 13, 23, 43 °C

Sample	Parameter	Temperature, °C					
		13		23		43	
		PLLA	PLLA/Starch	PLLA	PLLA/Starch	PLLA	PLLA/Starch
T1R4	$K_{p,s}$	0.33 ± 0.02 ^a	0.25 ± 0.02 ^a	2.48 ± 0.09 ^a	0.0029 ± 0.0007 ^a	0.011 ± 0.001 ^a	0.0018 ± 0.0005 ^a
	α	502.1	534.4	66.1	46350.4	14536.9	72793.9
T2R3	$K_{p,s}$	3.66 ± 0.13 ^b	n/a	4.02 ± 0.20 ^b	n/a	0.008 ± 0.002 ^b	n/a
	α	36.1	n/a	32.5	n/a	17229.0	n/a
T2R2	$K_{p,s}$	11.62 ± 1.06 ^c	0.86 ± 0.06 ^b	4.27 ± 0.08 ^b	0.0113 ± 0.0027 ^b	0.004 ± 0.000 ^c	0.0007 ± 0.0001 ^b
	α	12.0	146.1	32.5	10997.1	37779.3	178394.2
T3R2	$K_{p,s}$	6.52 ± 0.48 ^d	n/a	3.61 ± 0.24 ^b	n/a	0.007 ± 0.002 ^b	n/a
	α	21.6	n/a	38.6	n/a	18660.7	n/a
T4R1	$K_{p,s}$	40.37 ± 2.13 ^e	2.17 ± 0.24 ^c	7.50 ± 0.77 ^c	0.672 ± 0.026 ^c	0.018 ± 0.001 ^d	0.0015 ± 0.0003 ^{ab}
	α	3.55	57.0	18.9	182.2	7704.7	77723.8
T5R0	$K_{p,s}$	n/a	4.00 ± 0.11 ^d	n/a	1.297 ± 0.173 ^d	n/a	0.0024 ± 0.0005 ^c
	α	n/a	32.1	n/a	98.1	n/a	50917.9

Values in the same column with different superscript letters were significantly different at $\alpha = 0.05$; All of the values are expressed as average values and standard error.

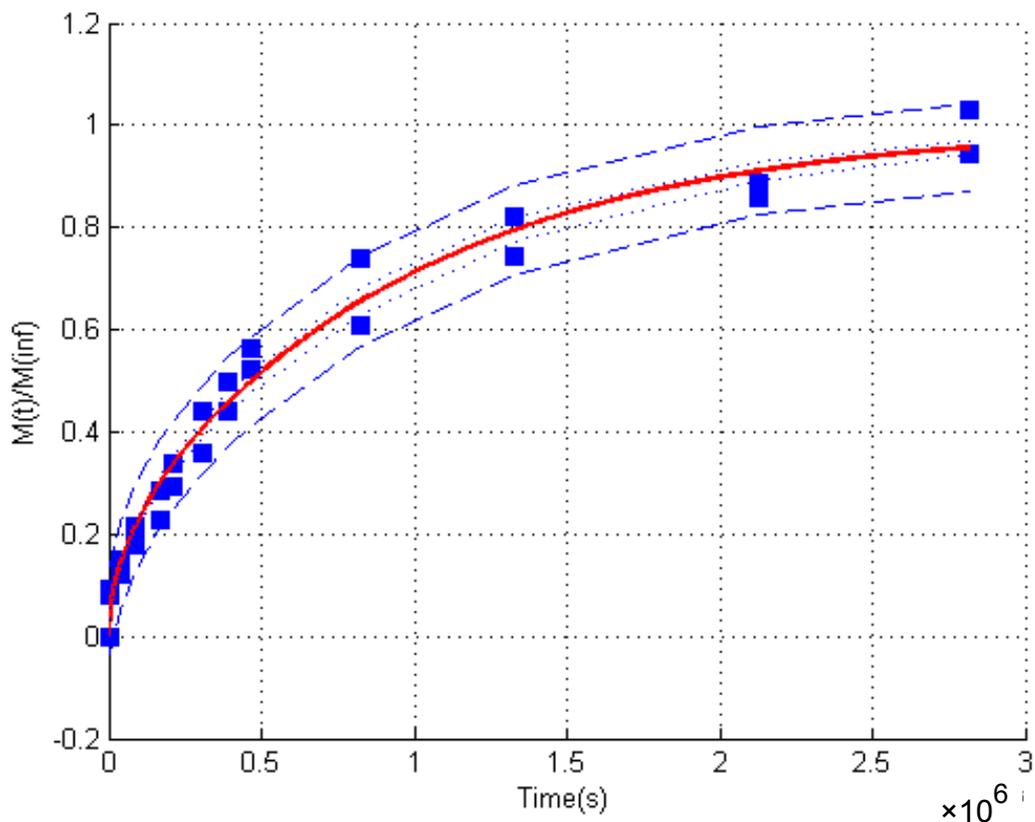
Table 6.6 Partition Coefficient ($K_{p,s}$) of Resveratrol from PLLA and PLLA/starch blend films into Ethanol at 13, 23, 43 °C

Sample	Parameter	Temperature, °C					
		13		23		43	
		PLLA	PLLA/Starch	PLLA	PLLA/Starch	PLLA	PLLA/Starch
T0R5	$K_{p,s}$	n/a	0.13 ± 0.01 ^a	n/a	0.075 ± 0.007 ^a	n/a	0.043 ± 0.005 ^a
	α	n/a	908.5	n/a	1415.4	n/a	2658.3
T1R4	$K_{p,s}$	1.11 ± 0.03 ^a	0.31 ± 0.02 ^b	1.22 ± 0.01 ^a	0.039 ± 0.006 ^b	0.016 ± 0.003 ^a	0.038 ± 0.007 ^a
	α	149.5	438.4	134.6	3470.5	10013.1	3415.0
T2R3	$K_{p,s}$	0.85 ± 0.03 ^b	n/a	0.93 ± 0.08 ^b	n/a	0.025 ± 0.006 ^a	n/a
	α	155.9	n/a	140.8	n/a	5198.3	n/a
T2R2	$K_{p,s}$	2.13 ± 0.02 ^c	0.51 ± 0.07 ^c	0.92 ± 0.18 ^b	0.050 ± 0.004 ^b	0.030 ± 0.011 ^a	0.038 ± 0.008 ^a
	α	65.8	248.3	150.7	2502.8	4643.0	3189.8
T3R2	$K_{p,s}$	1.46 ± 0.07 ^d	n/a	0.37 ± 0.02 ^c	n/a	0.025 ± 0.002 ^a	n/a
	α	96.8	n/a	382.2	n/a	5525.5	n/a
T4R1	$K_{p,s}$	4.62 ± 0.29 ^e	1.10 ± 0.23 ^d	0.80 ± 0.04 ^b	0.147 ± 0.021 ^c	0.028 ± 0.005 ^a	0.063 ± 0.005 ^b
	α	31.0	112.6	177.4	833.1	5153.3	1904.1

Values in the same column with different superscript letters were significantly different at $\alpha = 0.05$; All of the values are expressed as average values and standard error.

6.3.7. Diffusion of α -TOC and resveratrol from PLLA and PLLA/starch blends film

Figure 6.9 a and b and 6.10 a and b show the diffusion of resveratrol and α -TOC from PLLA and PLLA/starch blend films into ethanol at three different temperatures. It was found, as expected, that the equilibration time decreased with increasing temperature between 13 and 43 °C due to the temperature dependence of diffusion. In PLLA films, equilibrium for resveratrol was reached after 167 and 14 h for all samples at 23 and 43 °C, respectively, except for T4R1 at 23 °C which did not reach equilibrium. Equilibrium was not reached for any samples at 13 °C. It was estimated using Eq (5) that the equilibrium would be reached at 49 (T1R4), 463 (T2R3), 509 (T2R2), 498 (T3R2), and 414 (T4R1) days, respectively, at 13 °C. For α -TOC, equilibrium was reached after 500 and 69 h at 23 and 43 °C, respectively. At 13 °C, equilibrium was not reached after 833 h; it was estimated that equilibrium would be reached after about 490 days except for T4R1 which would reach equilibrium at 89 days. For the PLLA/starch blend films, equilibrium for resveratrol was reached after approximately 416, 111, and 13 h at 13, 23 and 43 °C, respectively, except for T4R1, which reached equilibrium after about 555, 222, and 20 h, respectively. It can be seen that the movement of resveratrol with relatively low concentration could be hindered by the long chain α -TOC having higher concentration in PLLA/starch matrix. For α -TOC, equilibrium was reached after 388 and 50 h at 23 and 43 °C, respectively; at 13 °C, equilibrium was not reached after 777 h.

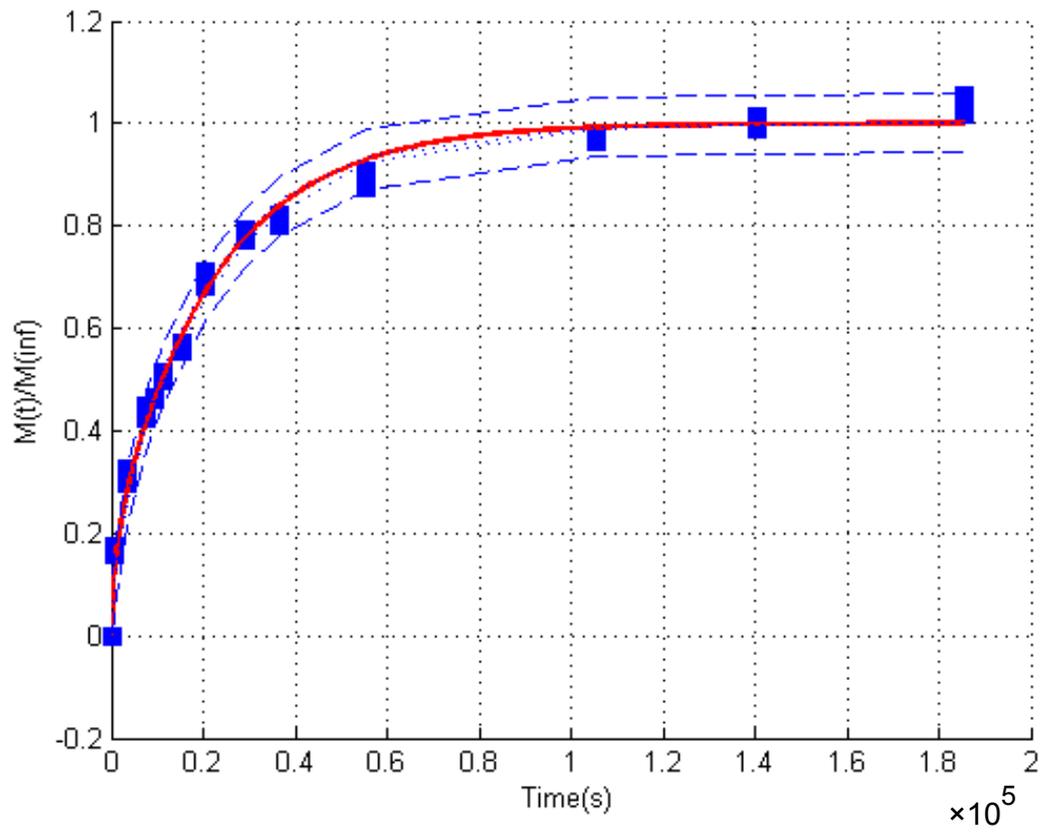


T1R4-RES 13°C

(a)

Figure 6.9 Diffusion of resveratrol (a) and α -TOC (b) from PLLA films to ethanol at 13, 23, 43 °C according to the Fick's second law. The y-axis is the ratio of the concentration of resveratrol and α -TOC in solution at time t to the concentration of resveratrol and α -TOC in solution at equilibrium (M_t/M_{eq}), and the x-axes are time (t) in s. The central line (red) shows the best fit to the experimental data, and the outer lines (blue) are the predicted intervals for the experimental values.

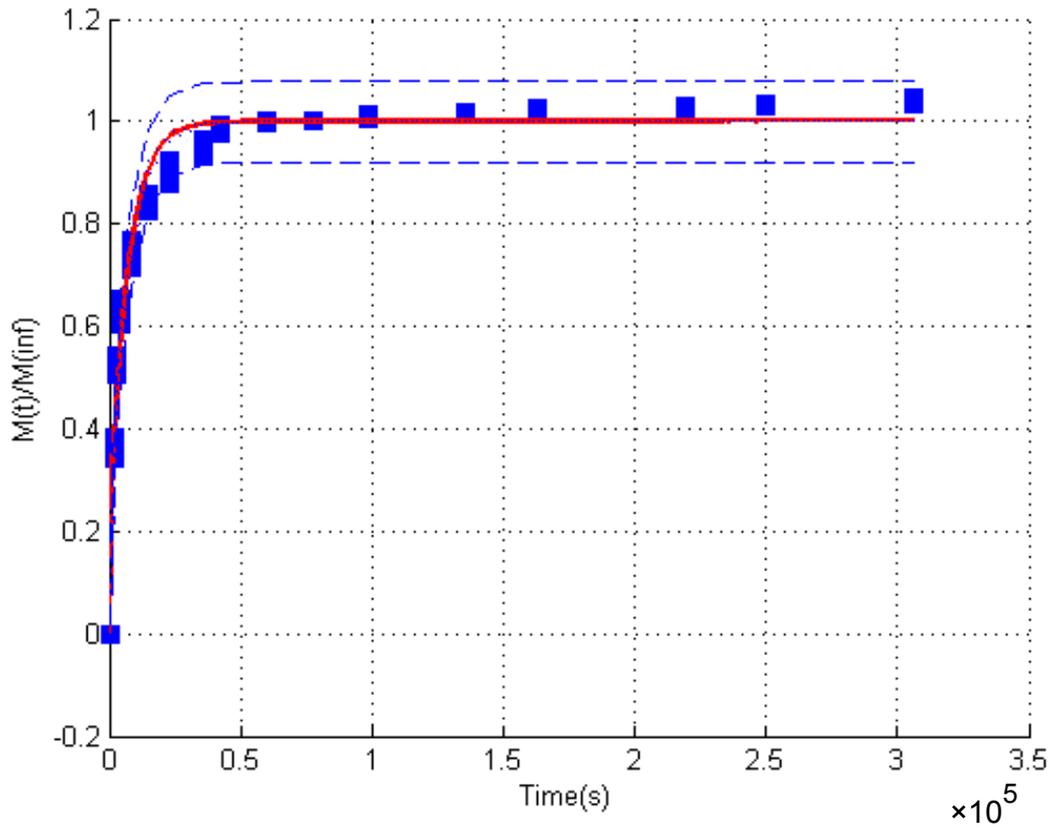
Figure 6.9 (cont'd)



T1R4-RES 23°C

(a)

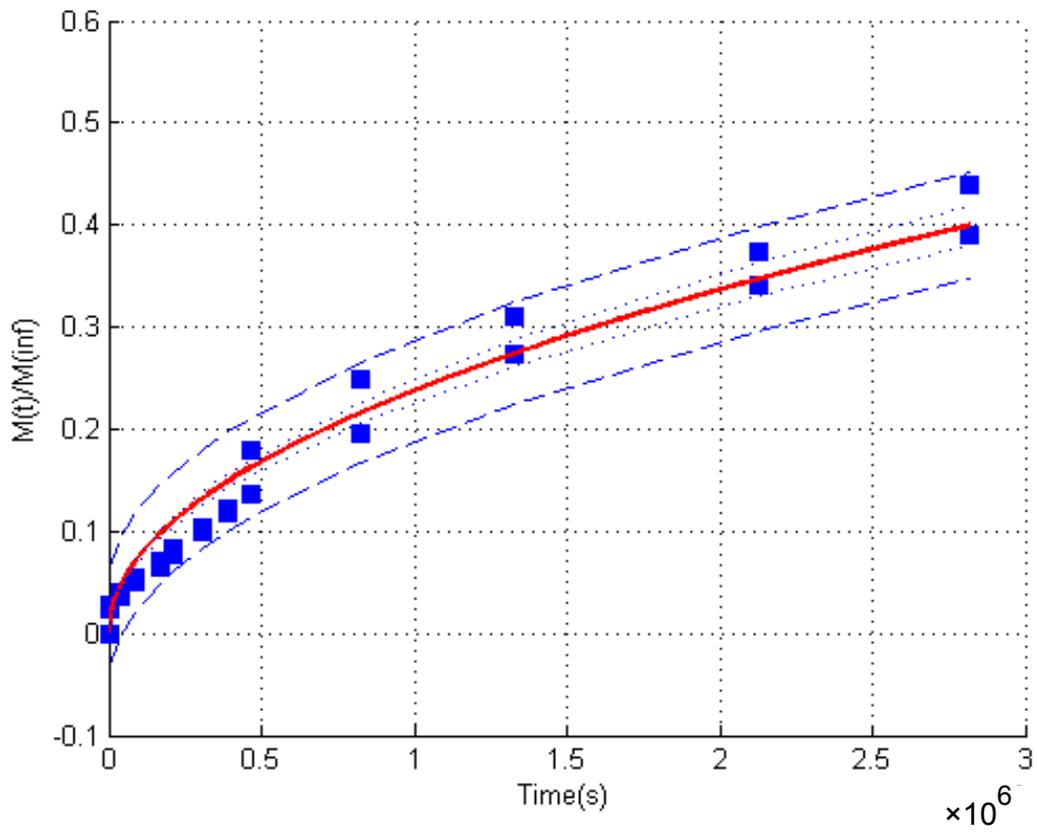
Figure 6.9 (cont'd)



T1R4-RES 43°C

(a)

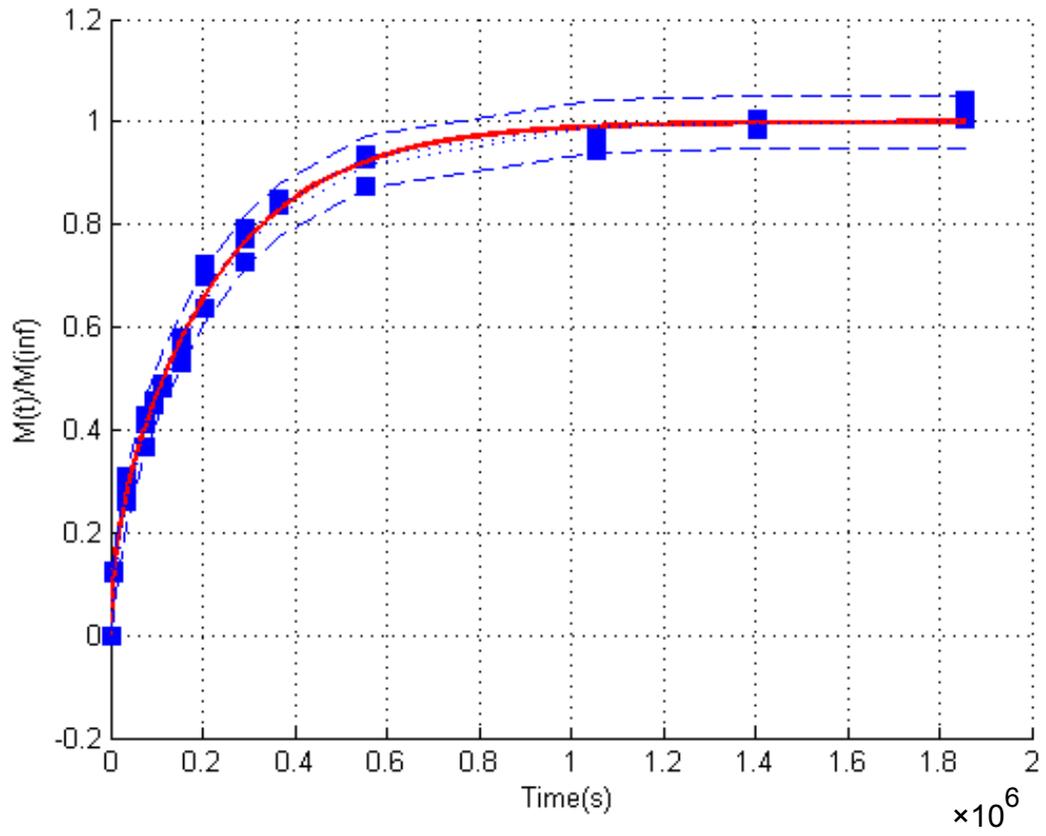
Figure 6.9 (cont'd)



T2R3-RES 13°C

(a)

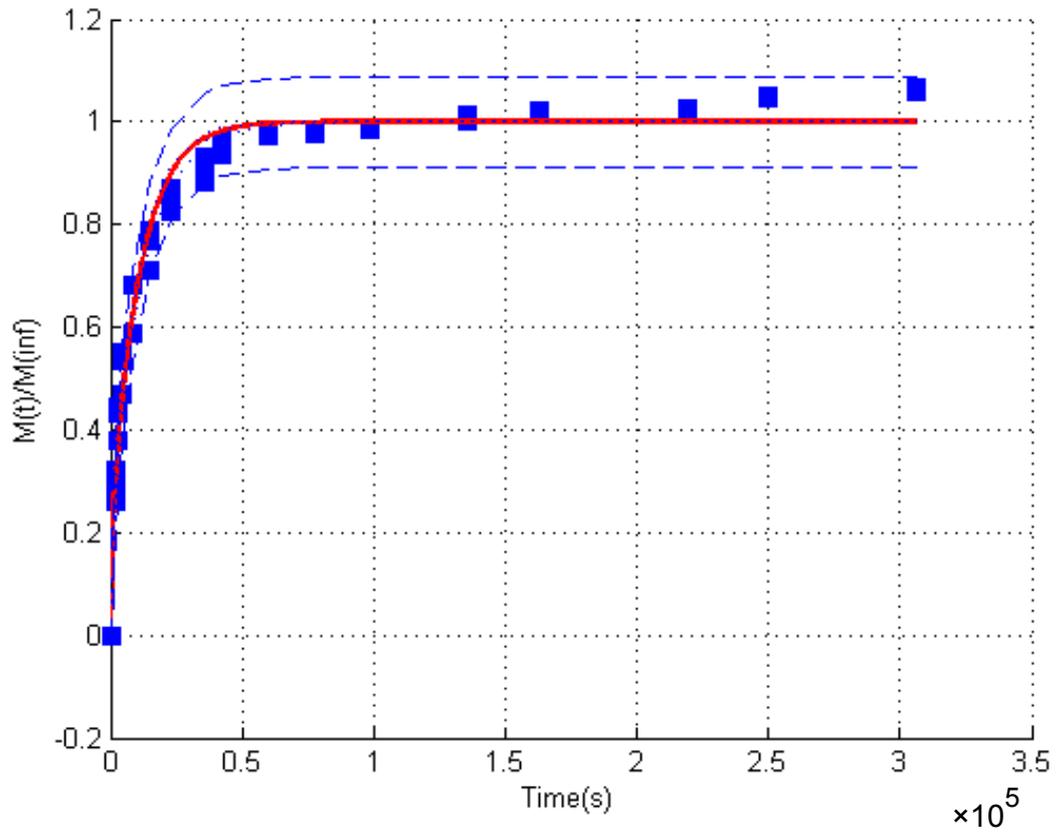
Figure 6.9 (cont'd)



T2R3-RES 23°C

(a)

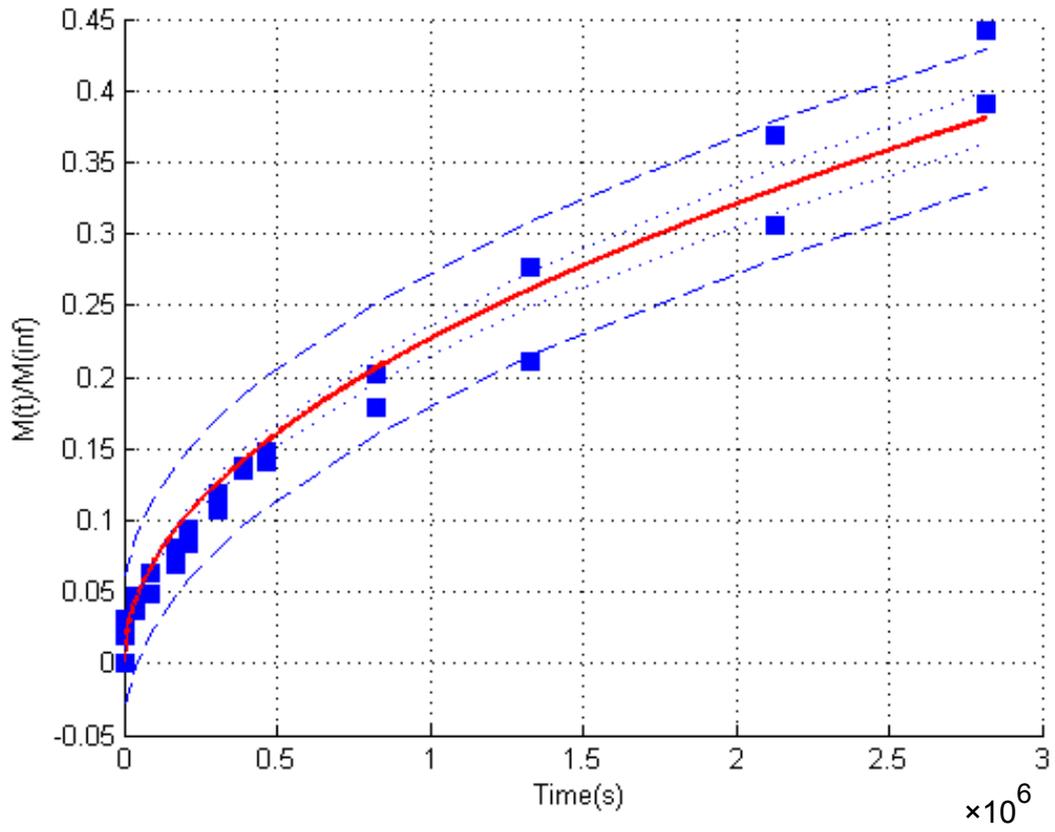
Figure 6.9 (cont'd)



T2R3-RES 43°C

(a)

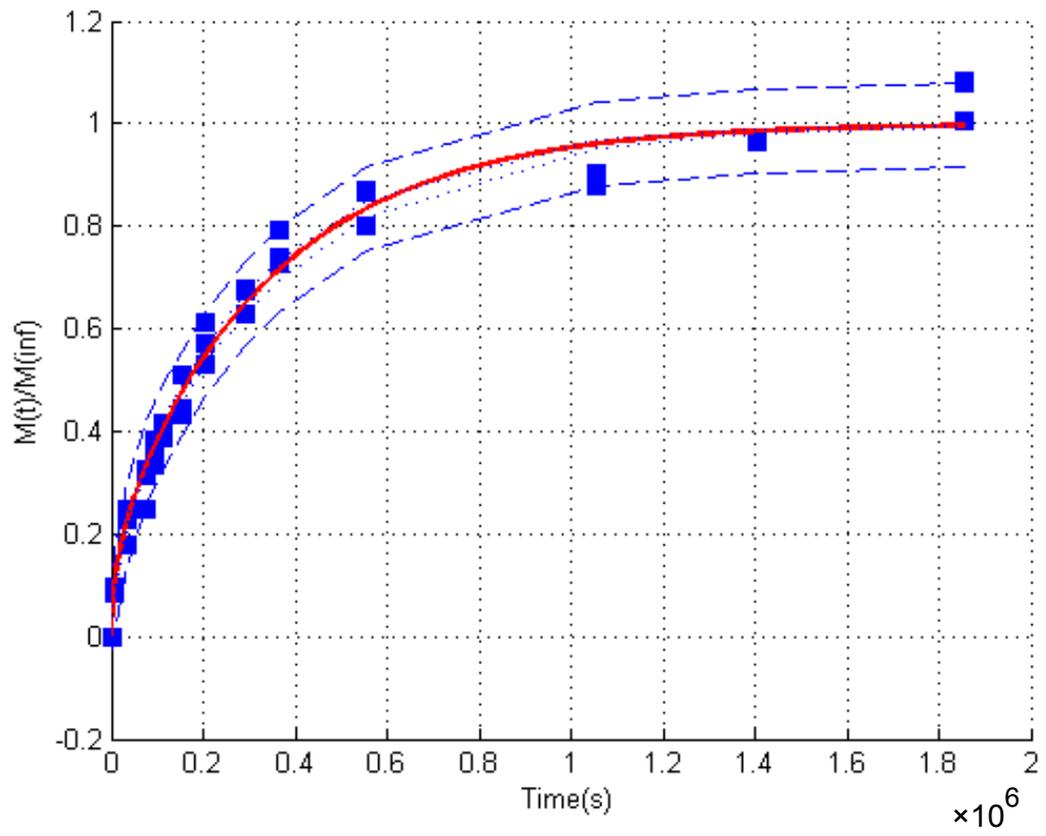
Figure 6.9 (cont'd)



T2R2-RES 13°C

(a)

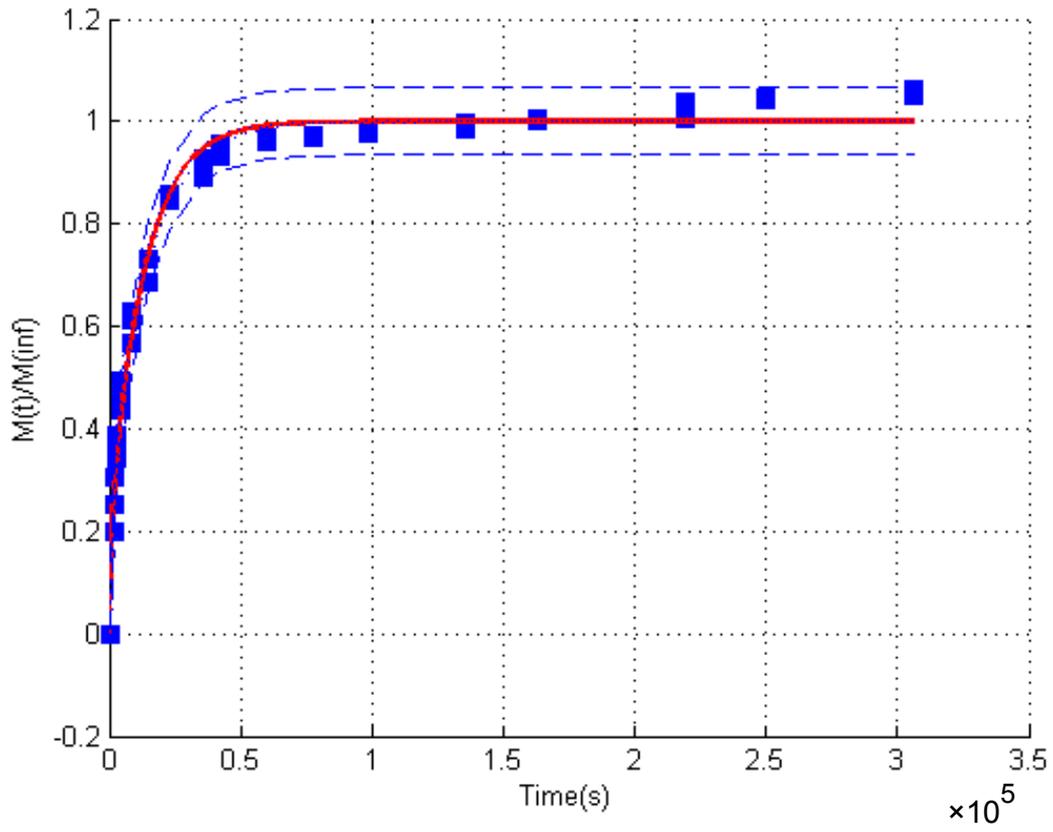
Figure 6.9 (cont'd)



T2R2-RES 23°C

(a)

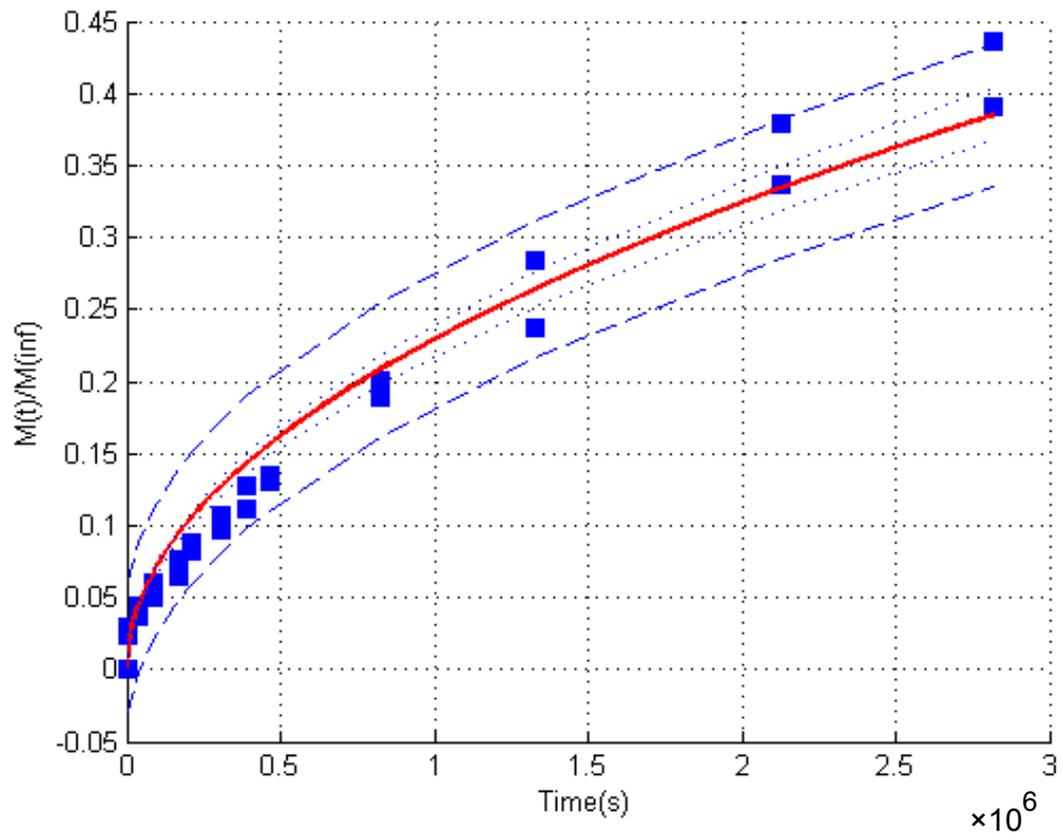
Figure 6.9 (cont'd)



T2R2-RES 43°C

(a)

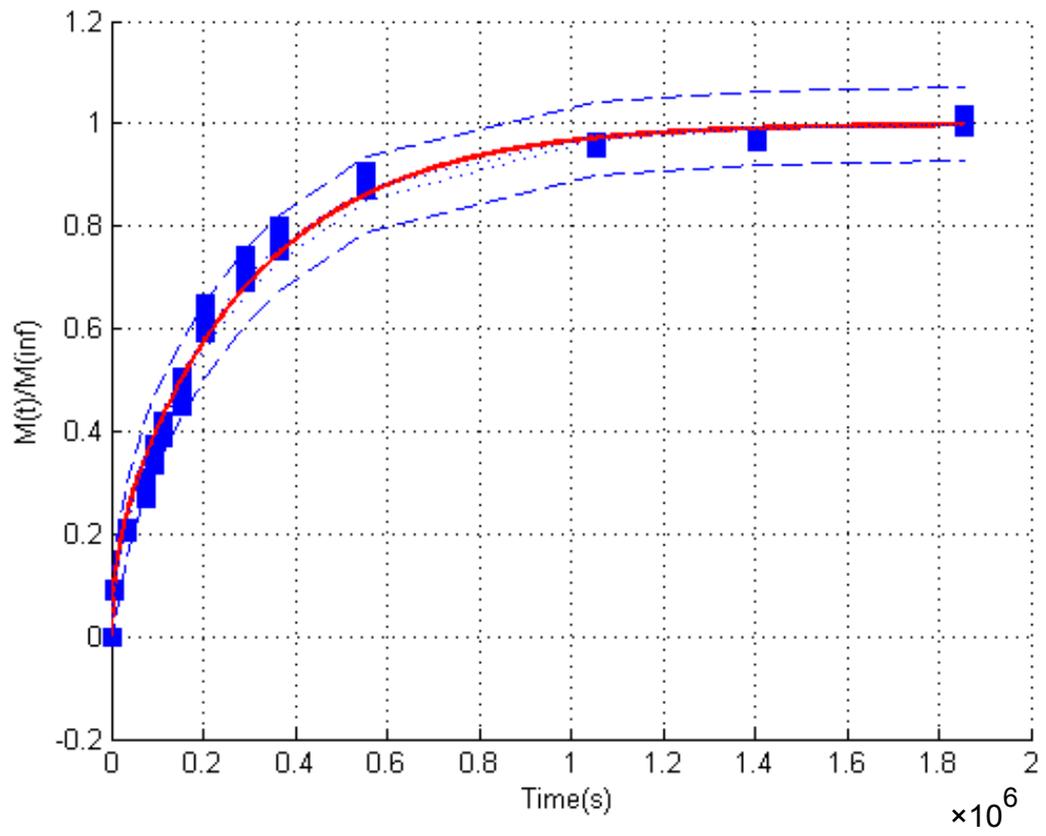
Figure 6.9 (cont'd)



T3R2-RES 13°C

(a)

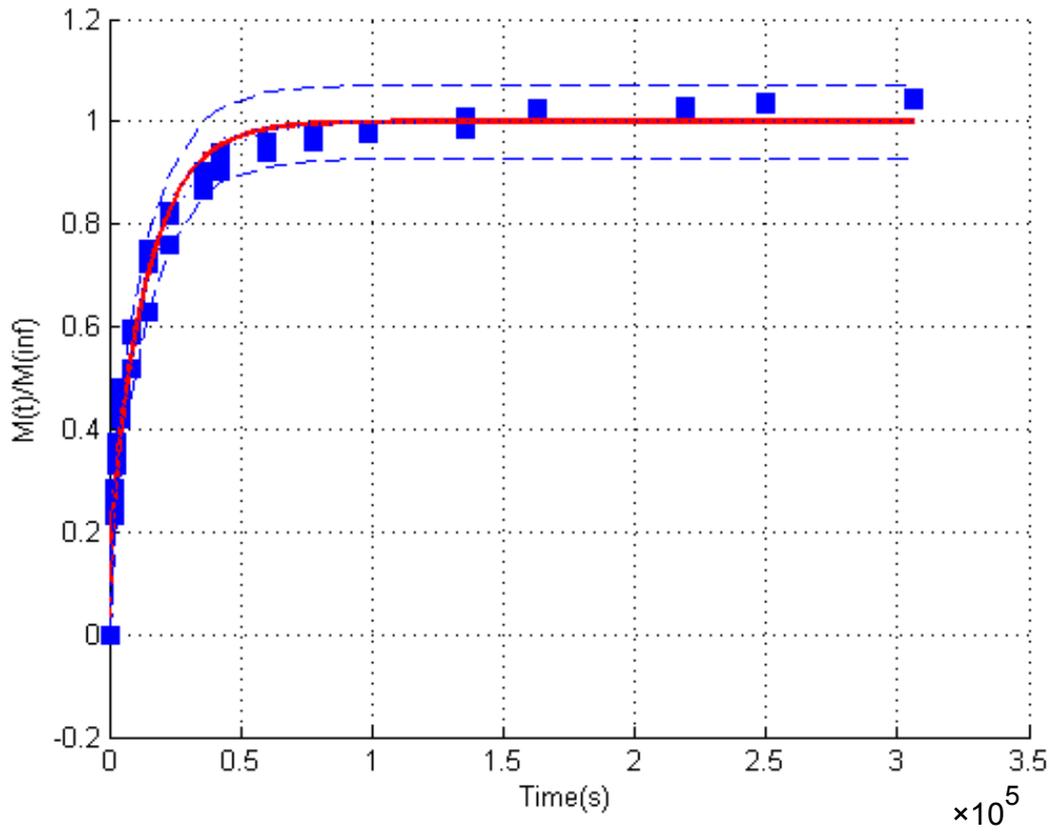
Figure 6.9 (cont'd)



T3R2-RES 23°C

(a)

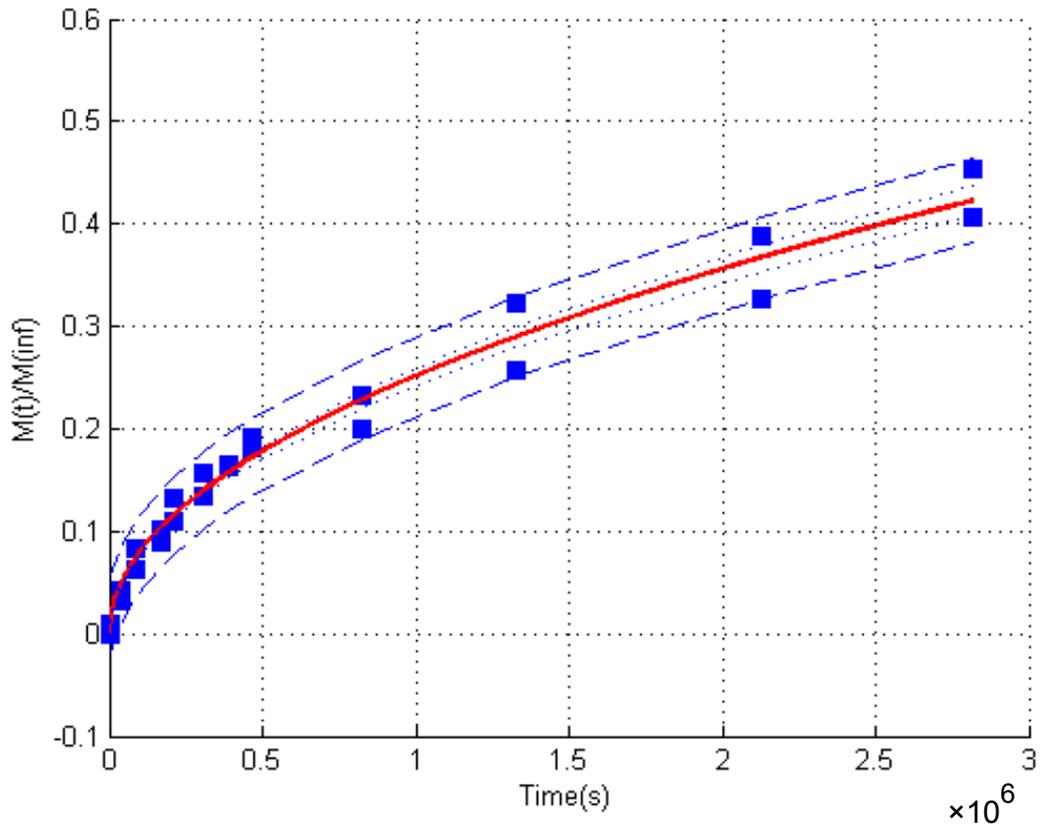
Figure 6.9 (cont'd)



T3R2-RES 43°C

(a)

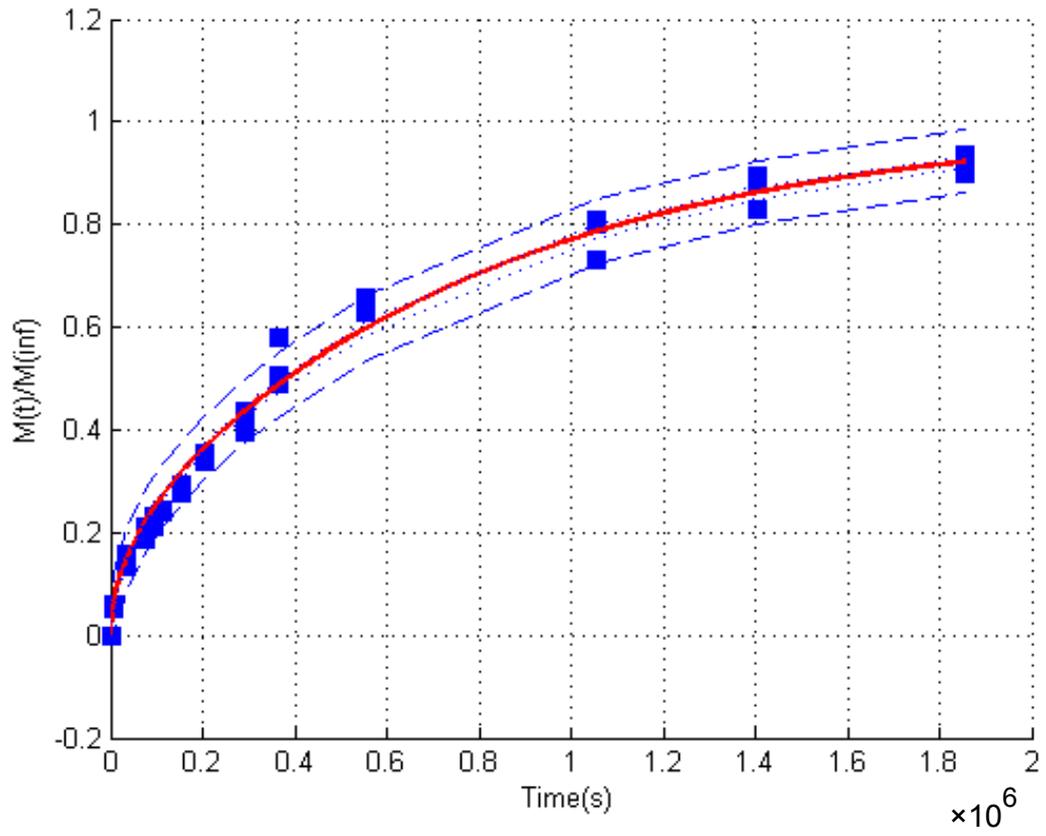
Figure 6.9 (cont'd)



T4R1-RES 13°C

(a)

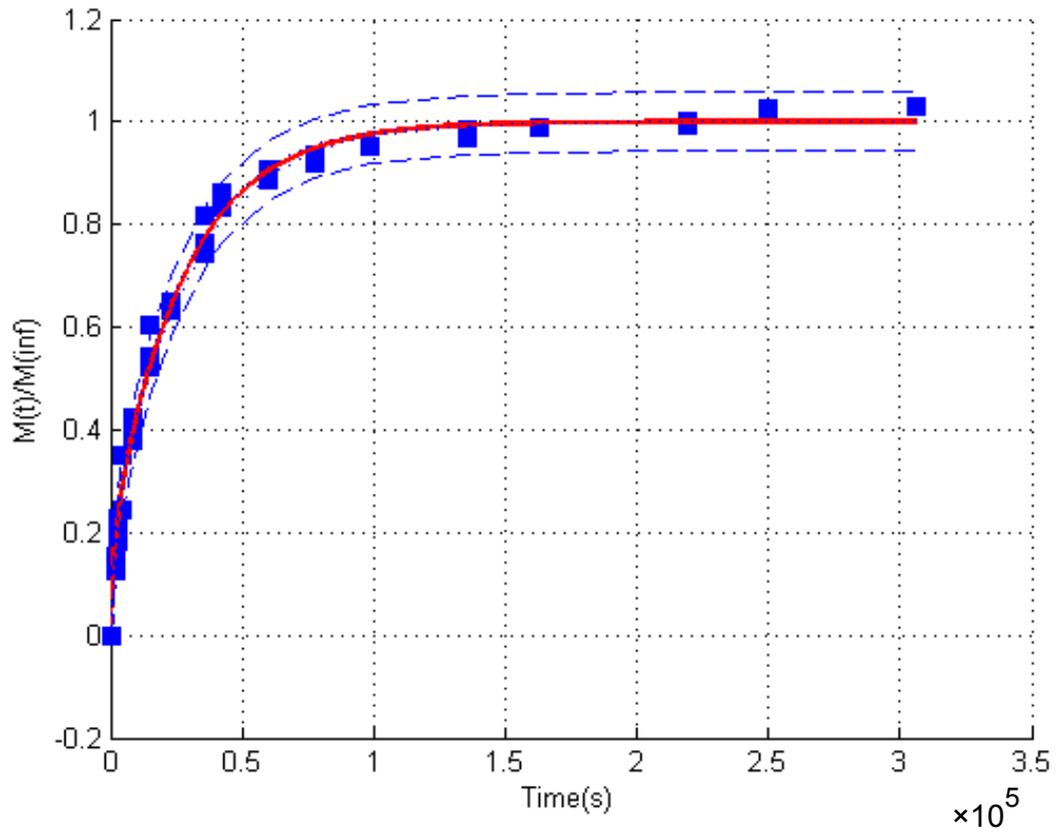
Figure 6.9 (cont'd)



T4R1-RES 23°C

(a)

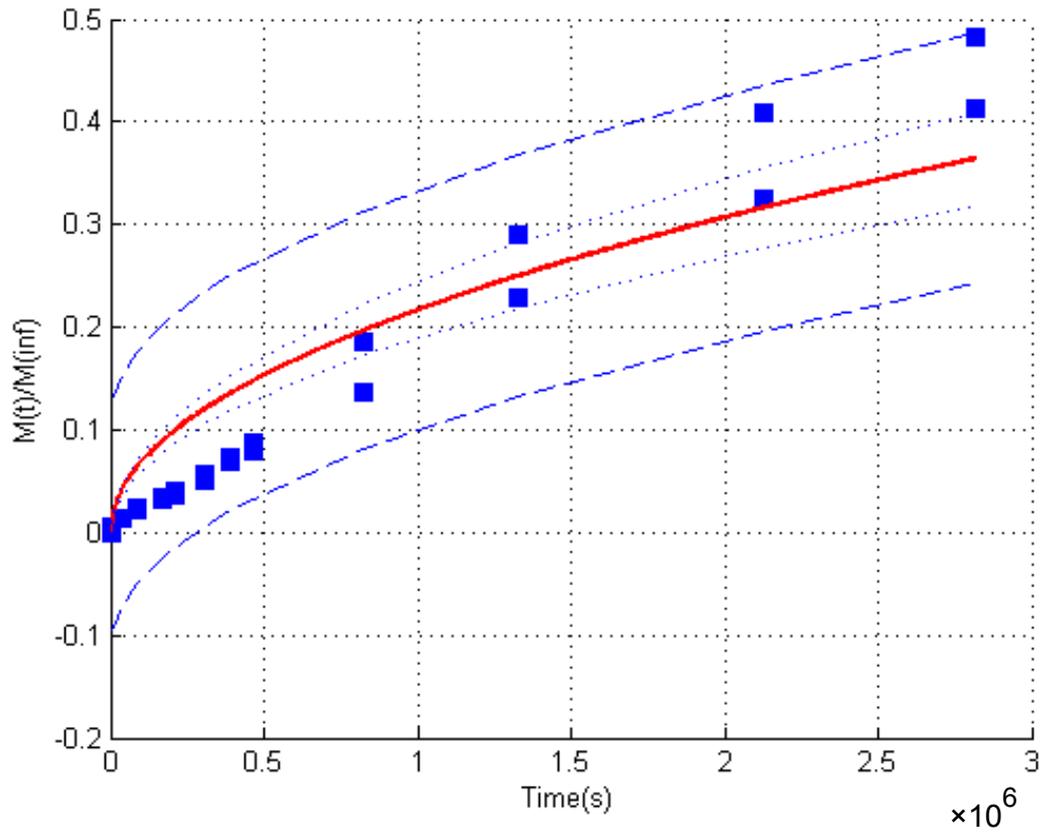
Figure 6.9 (cont'd)



T4R1-RES 43°C

(a)

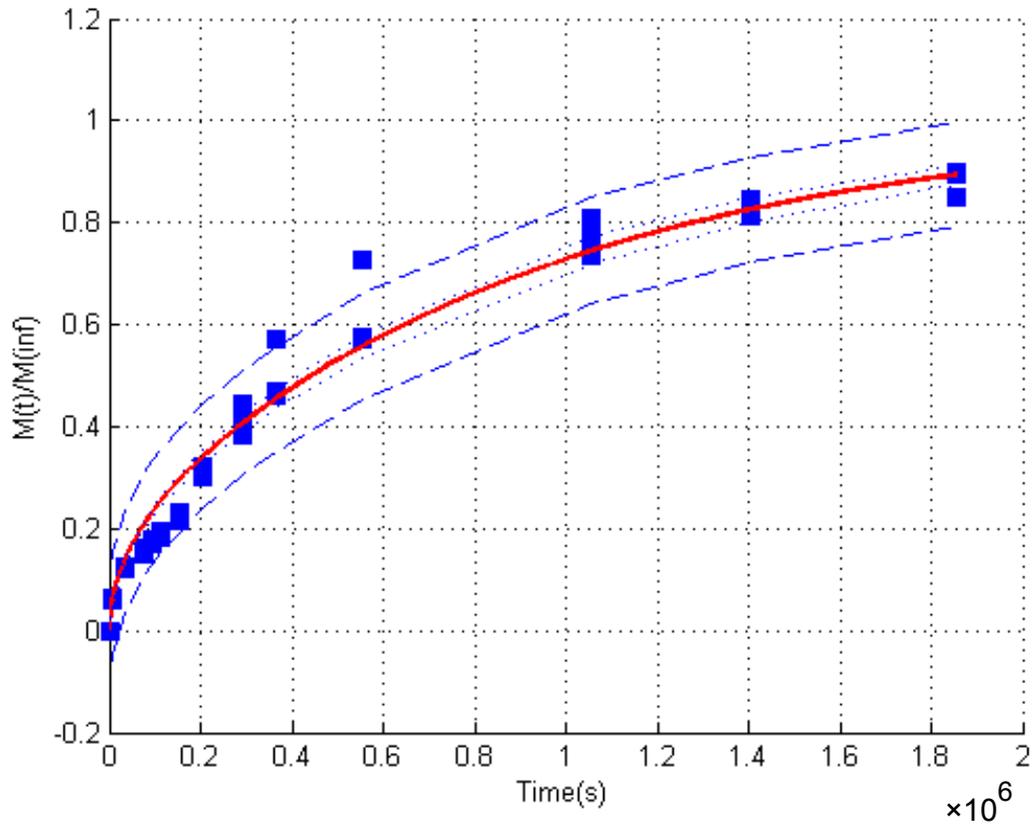
Figure 6.9 (cont'd)



T1R4-TOC 13°C

(b)

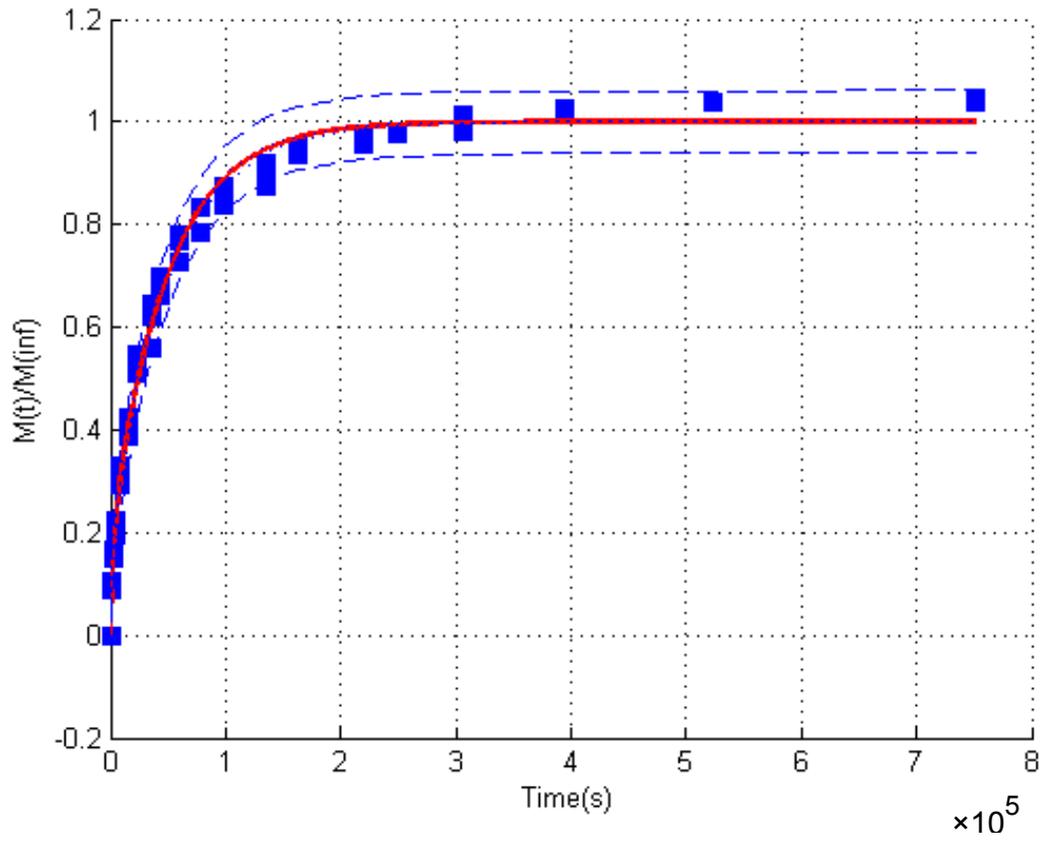
Figure 6.9 (cont'd)



T1R4-TOC 23°C

(b)

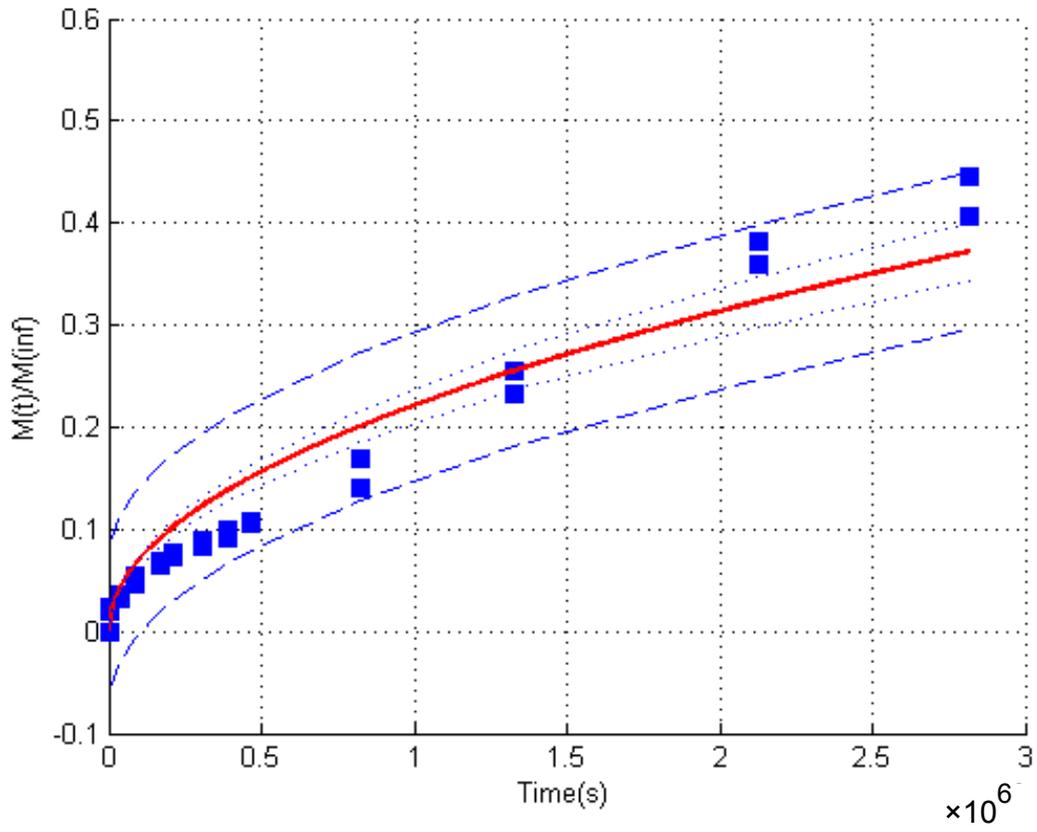
Figure 6.9 (cont'd)



T1R4-TOC 43°C

(b)

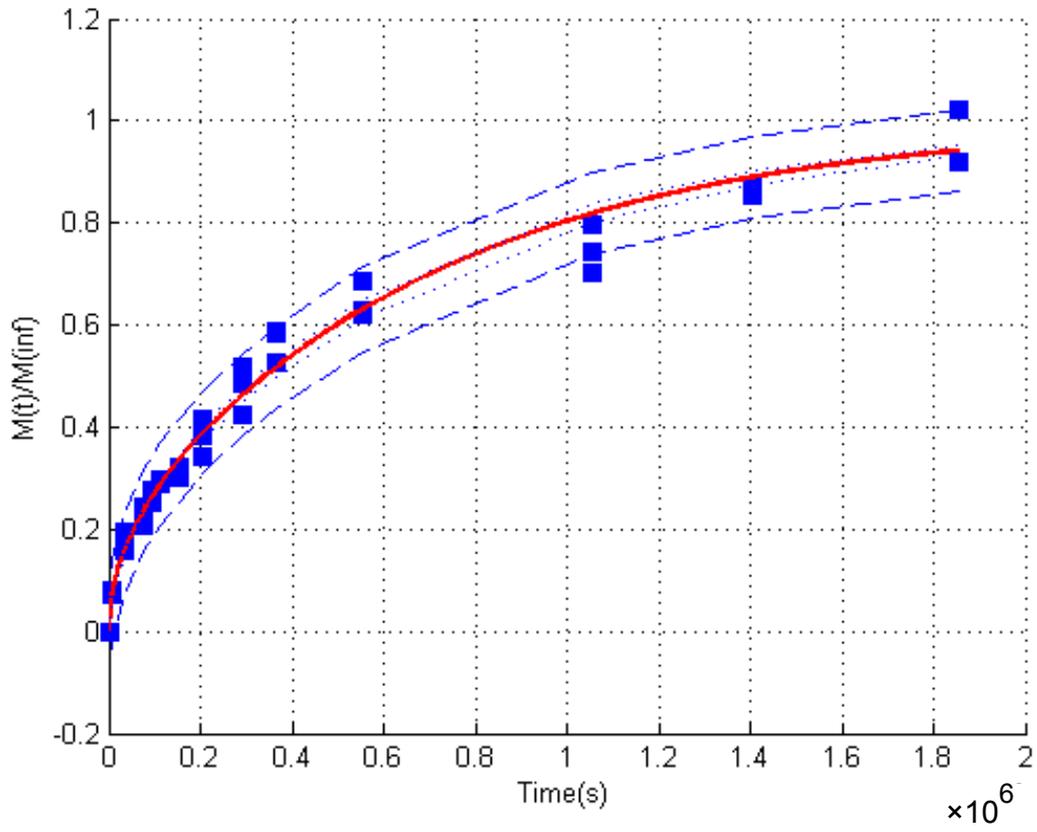
Figure 6.9 (cont'd)



T2R3-TOC 13°C

(b)

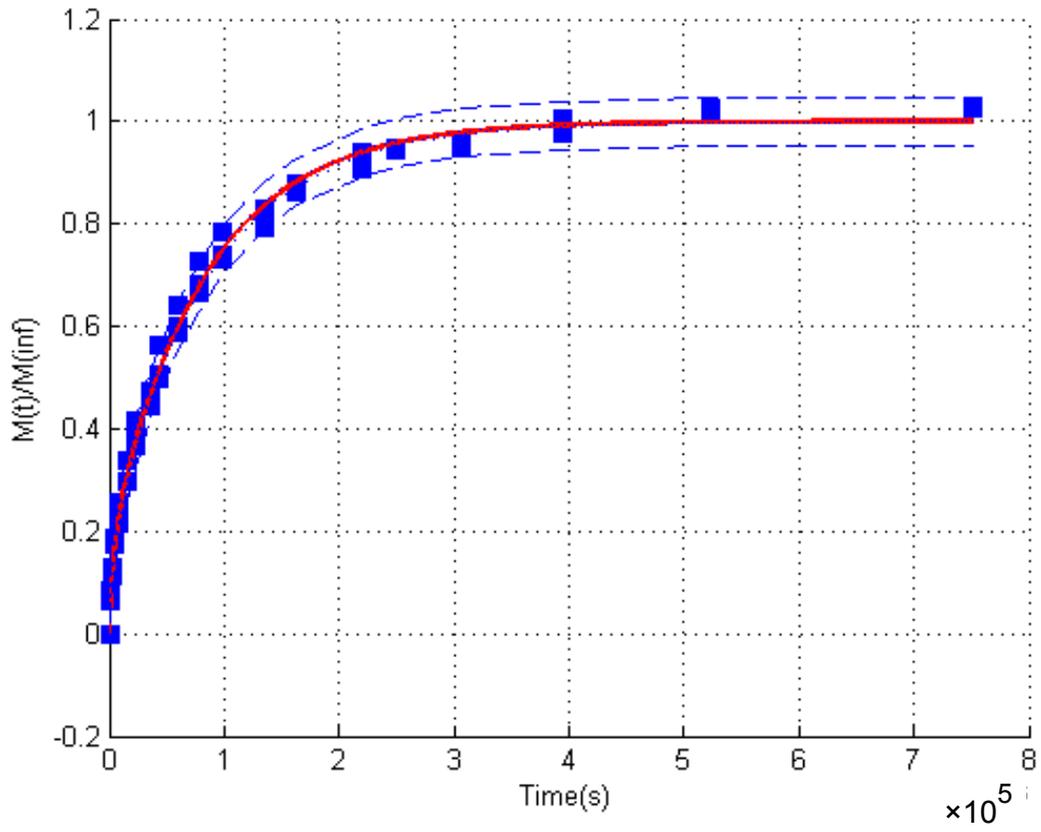
Figure 6.9 (cont'd)



T2R3-TOC 23°C

(b)

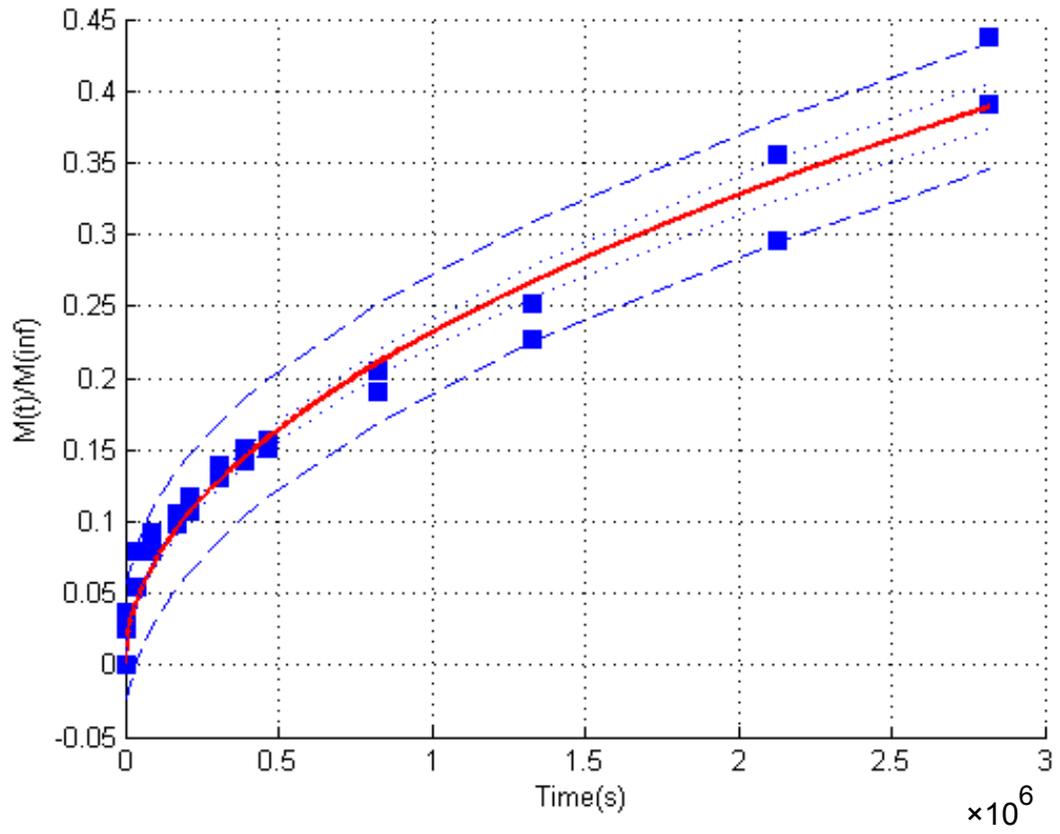
Figure 6.9 (cont'd)



T2R3-TOC 43°C

(b)

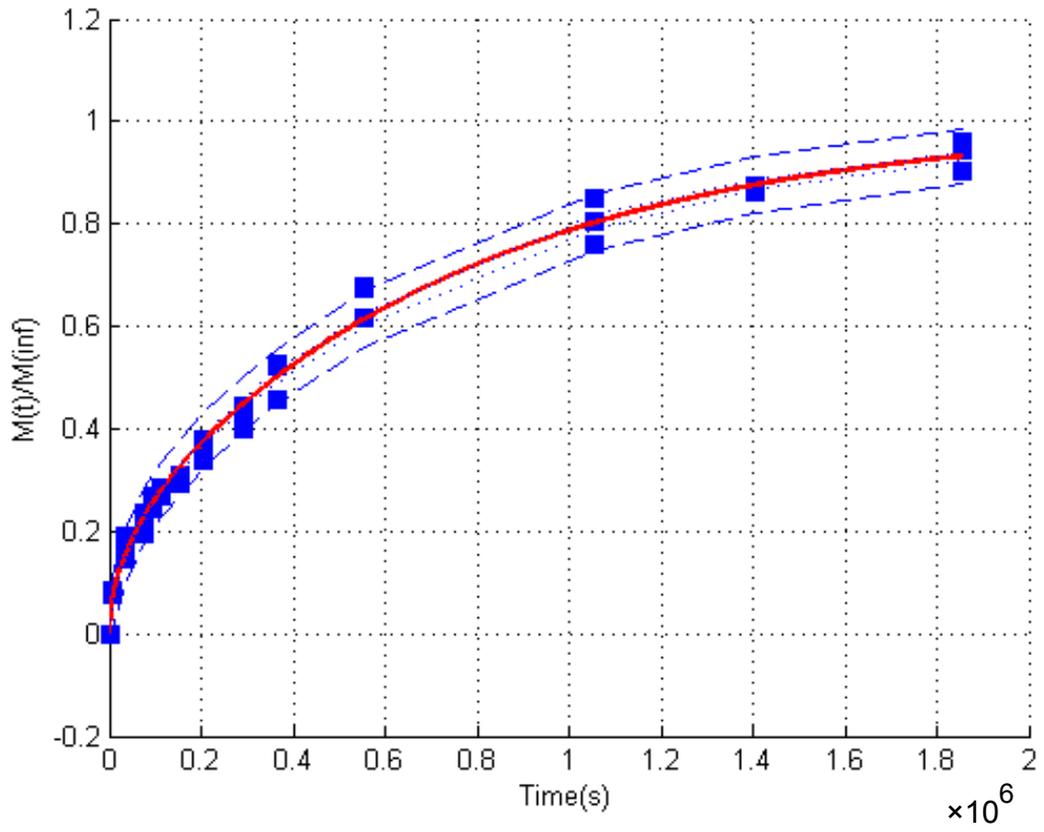
Figure 6.9 (cont'd)



T2R2-TOC 13°C

(b)

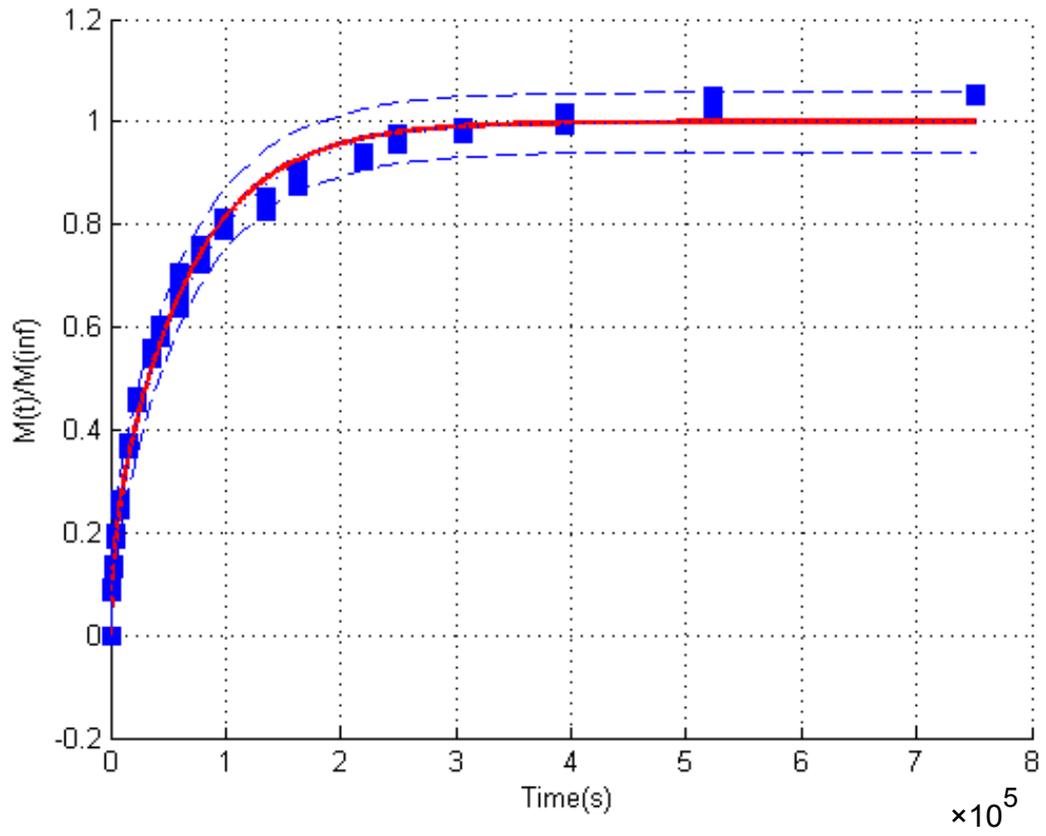
Figure 6.9 (cont'd)



T2R2-TOC 23°C

(b)

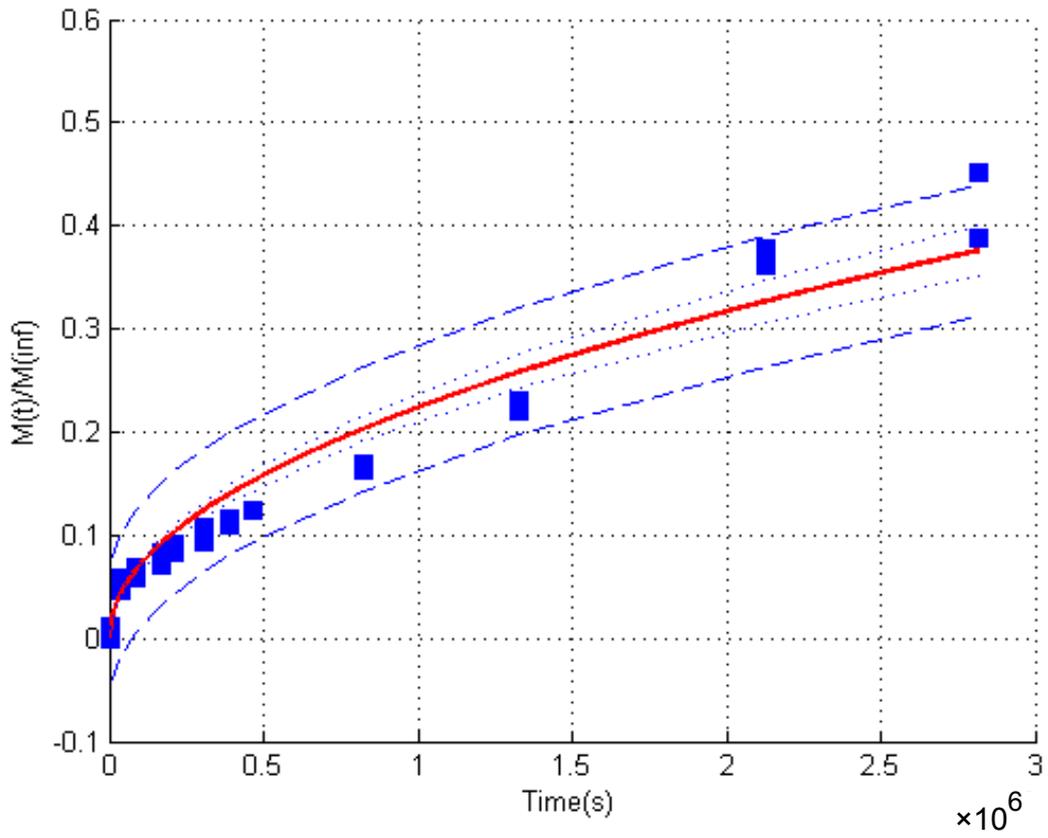
Figure 6.9 (cont'd)



T2R2-TOC 43°C

(b)

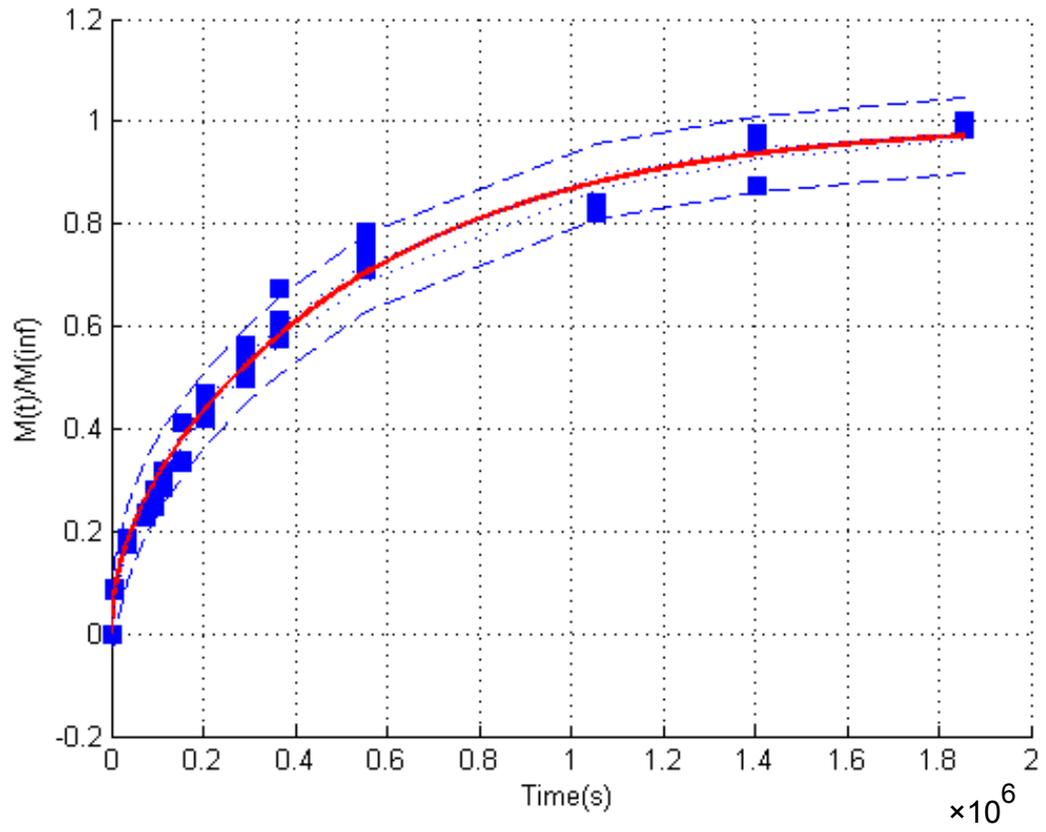
Figure 6.9 (cont'd)



T3R2-TOC 13°C

(b)

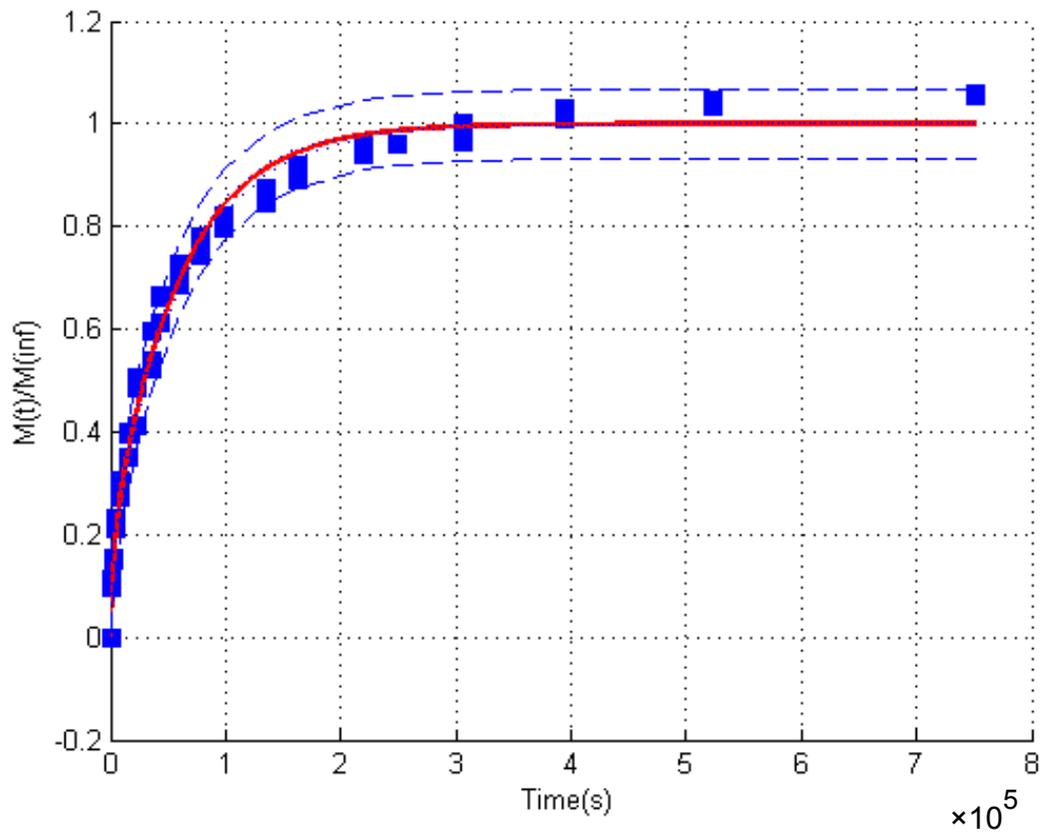
Figure 6.9 (cont'd)



T3R2-TOC 23°C

(b)

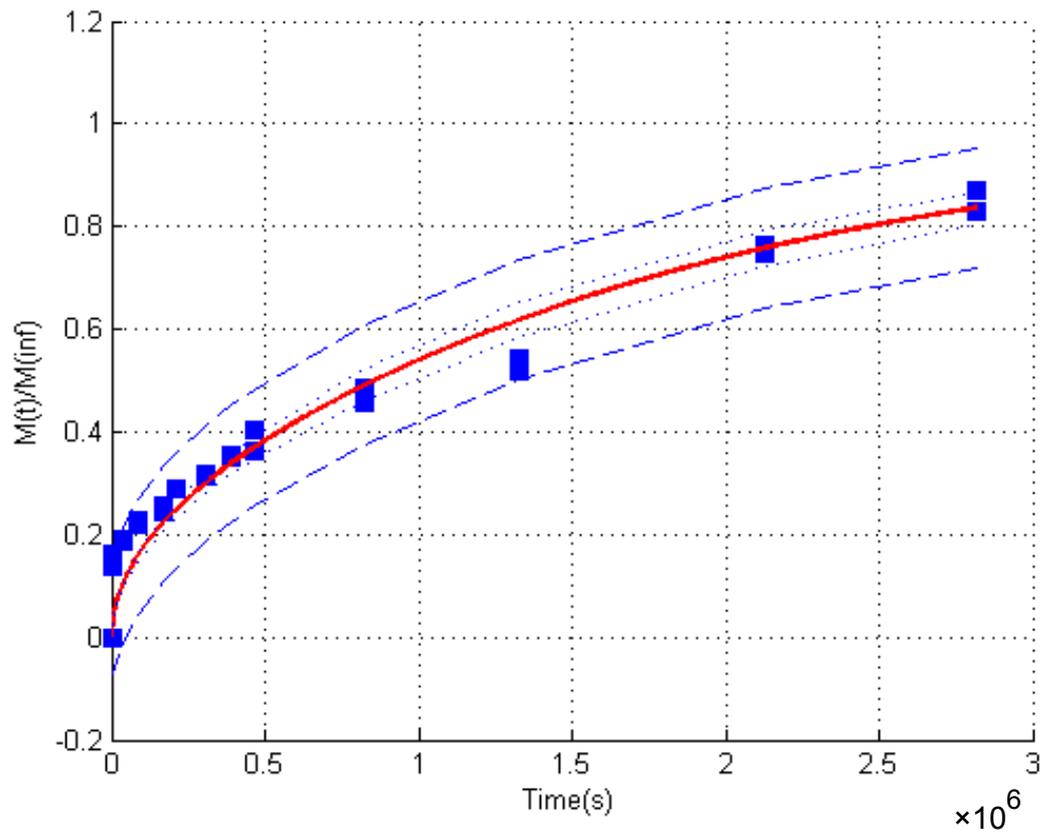
Figure 6.9 (cont'd)



T3R2-TOC 43°C

(b)

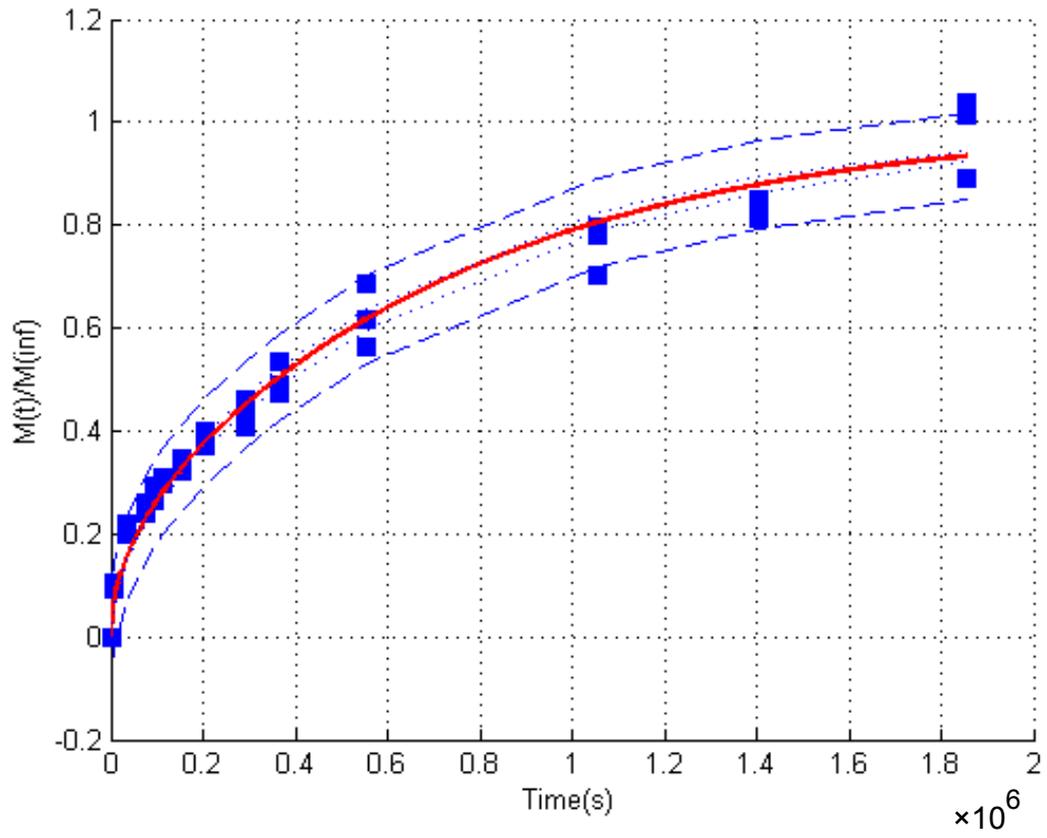
Figure 6.9 (cont'd)



T4R1-TOC 13°C

(b)

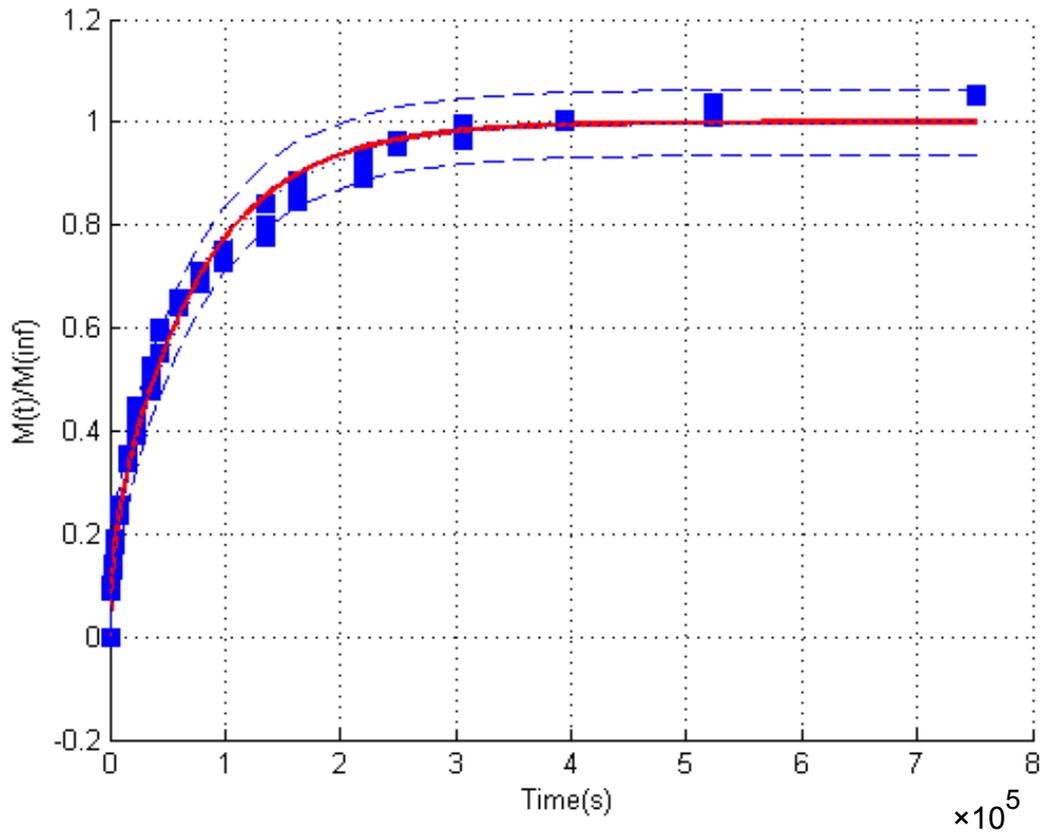
Figure 6.9 (cont'd)



T4R1-TOC 23°C

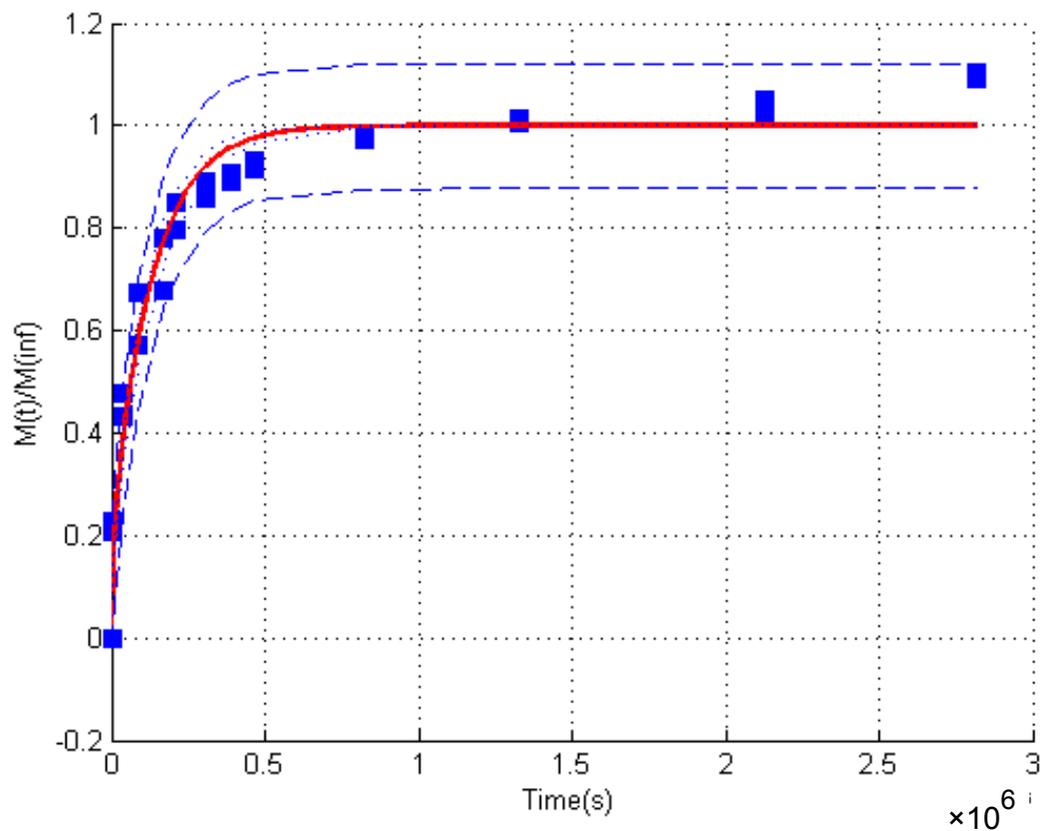
(b)

Figure 6.9 (cont'd)



T4R1-TOC 43°C

(b)

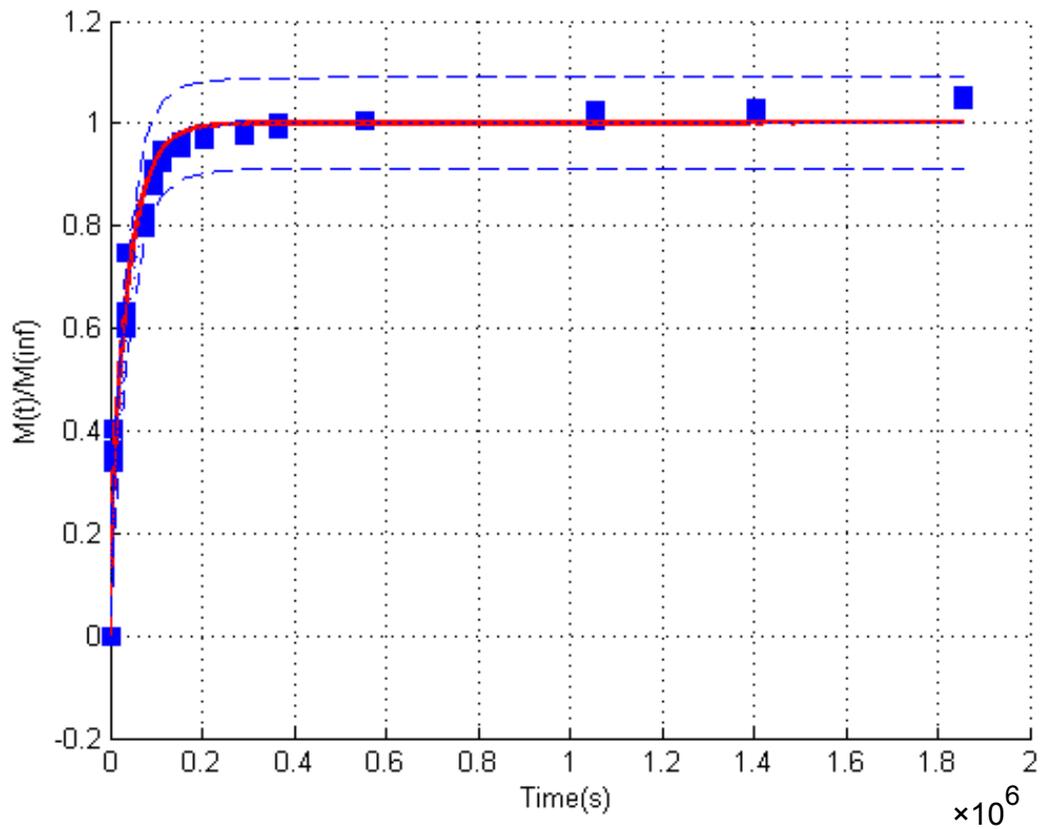


T0R5-RES 13°C

(a)

Figure 6.10 Diffusion of resveratrol (a) and α -TOC (b) from PLLA/starch blend films to ethanol at 13, 23, 43 °C according to the Fick's second law. The y-axis is the ratio of the concentration of resveratrol and α -TOC in solution at time t to the concentration of resveratrol and α -TOC in solution at equilibrium (M_t/M_{eq}), and the x-axes are time (t) in s. The central line (red) shows the best fit to the experimental data, and the outer lines (blue) are the predicted intervals for the experimental values.

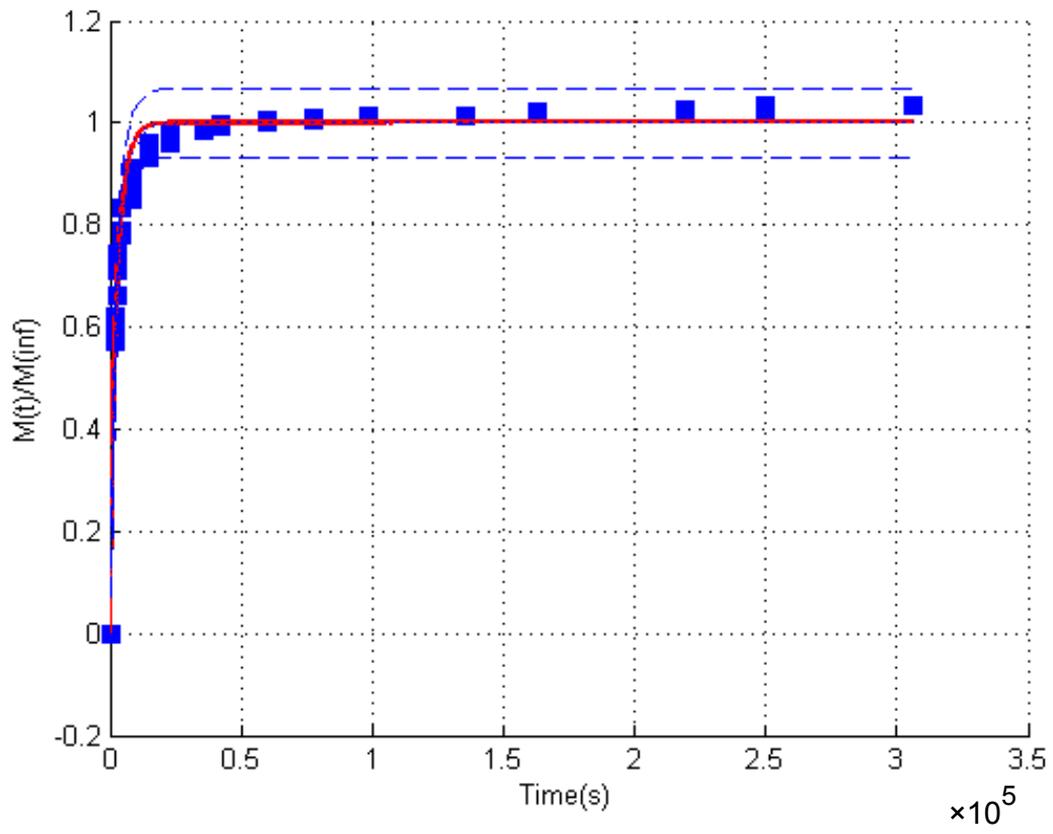
Figure 6.10 (cont'd)



T0R5-RES 23°C

(a)

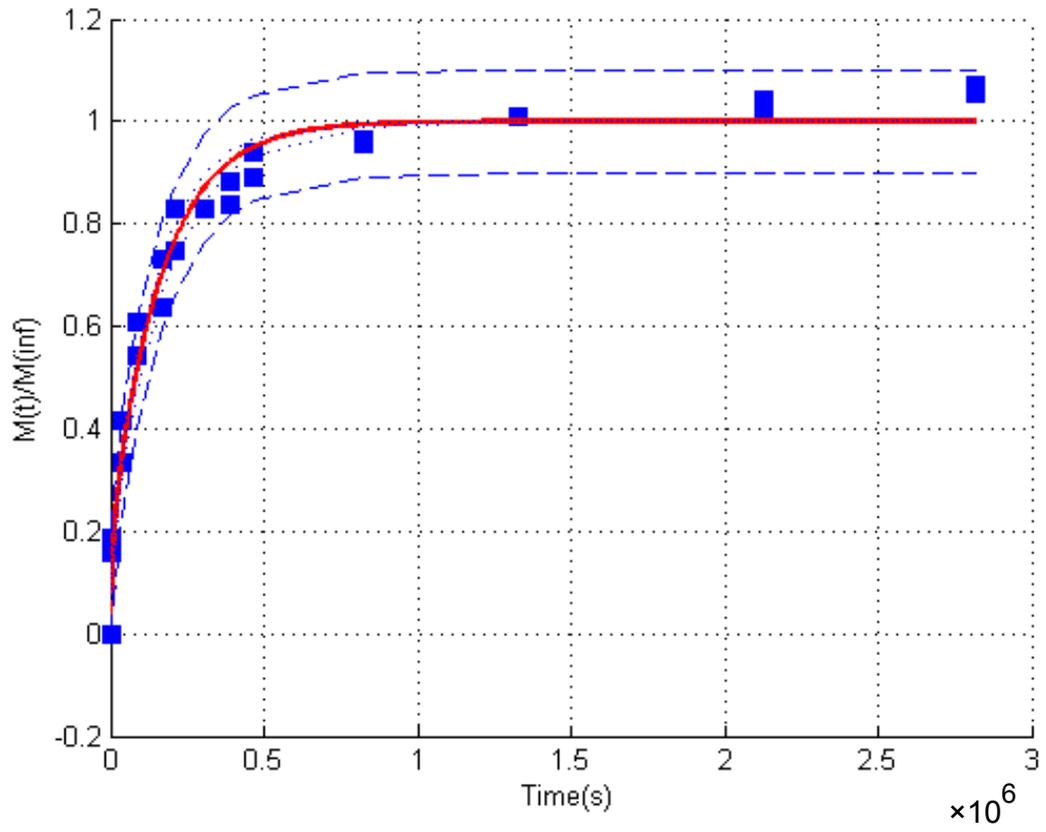
Figure 6.10 (cont'd)



T0R5-RES 43°C

(a)

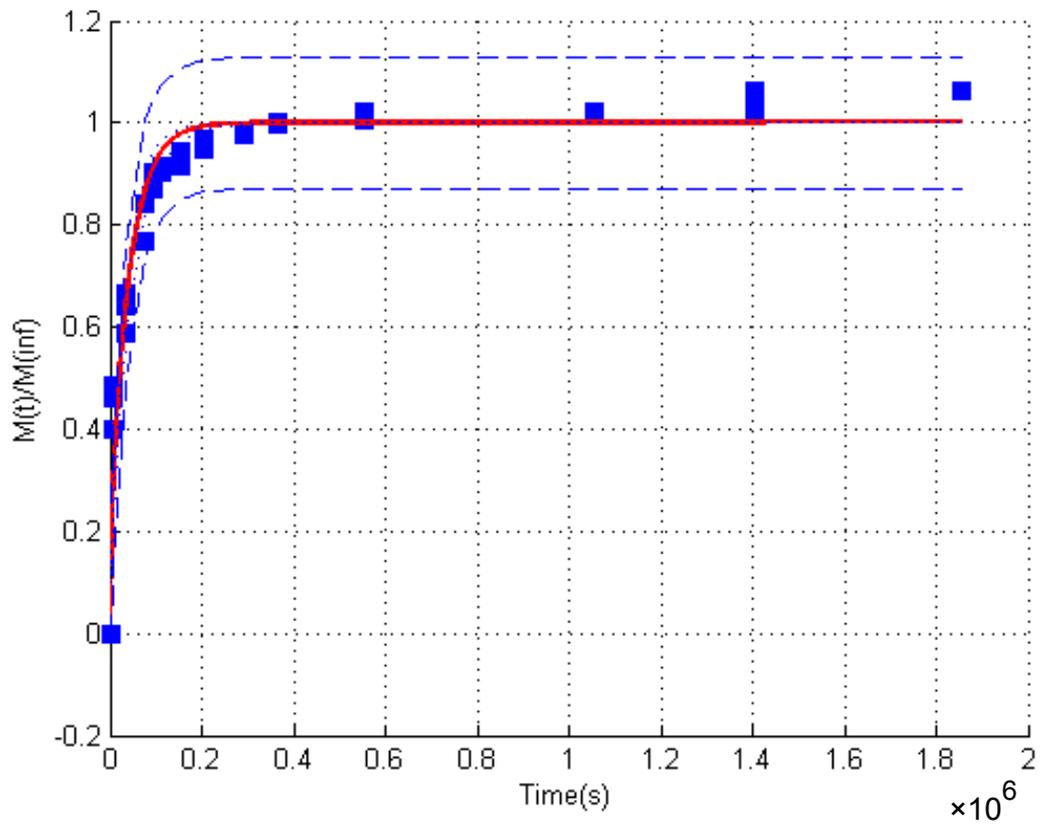
Figure 6.10 (cont'd)



T1R4-RES 13°C

(a)

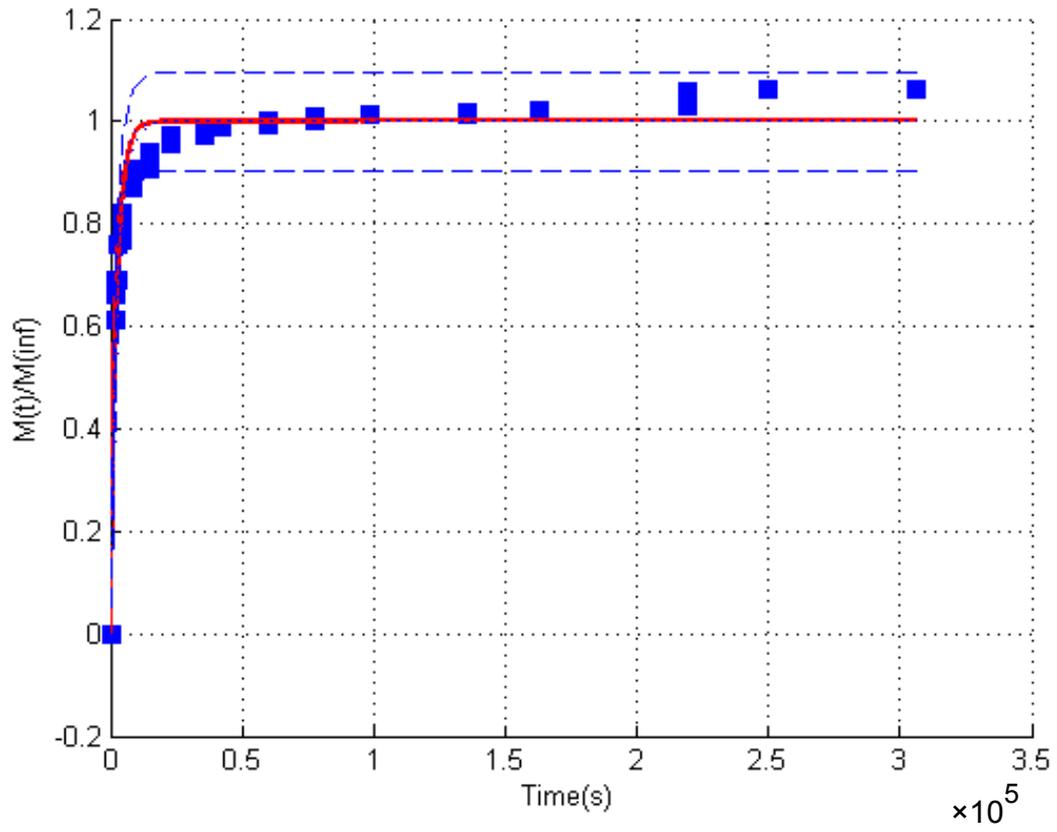
Figure 6.10 (cont'd)



T1R4-RES 23°C

(a)

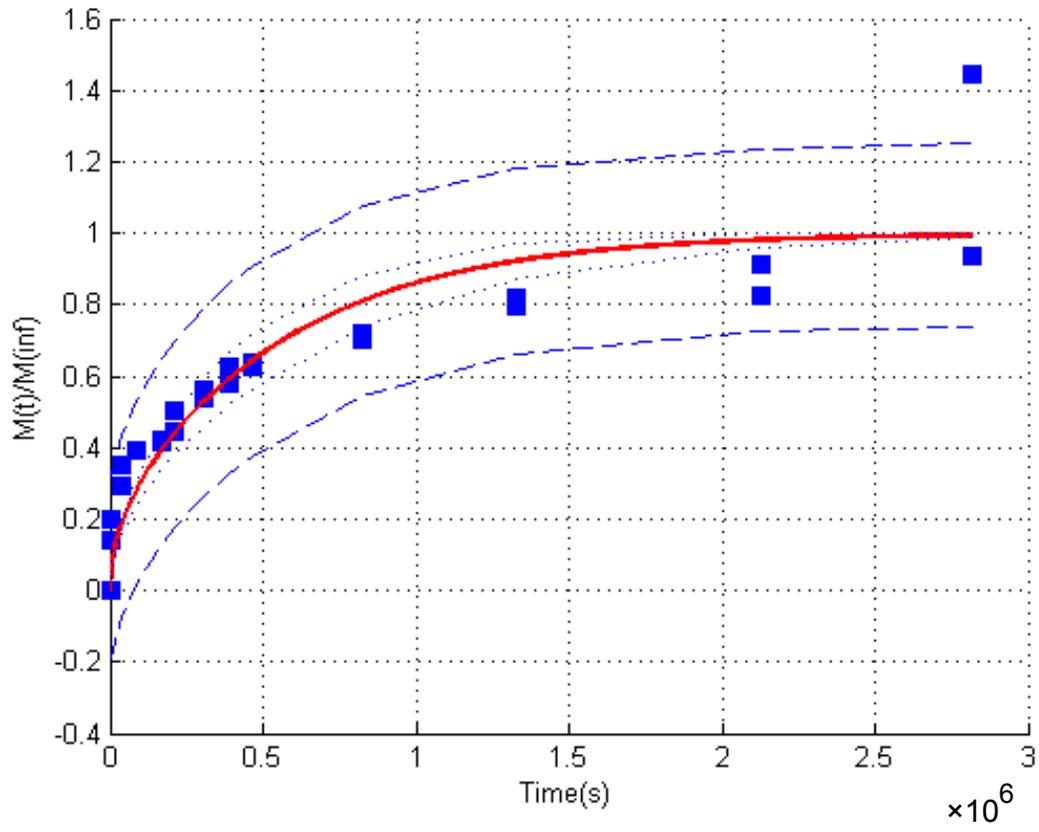
Figure 6.10 (cont'd)



T1R4-RES 43°C

(a)

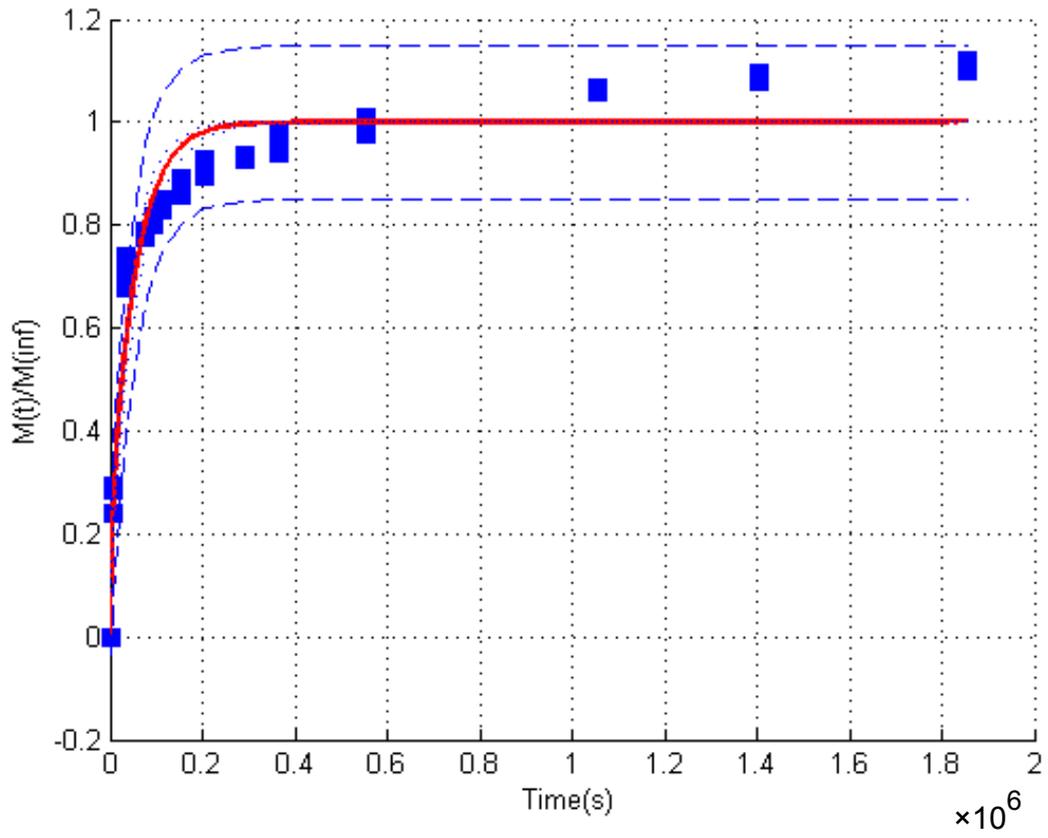
Figure 6.10 (cont'd)



T2R2-RES 13°C

(a)

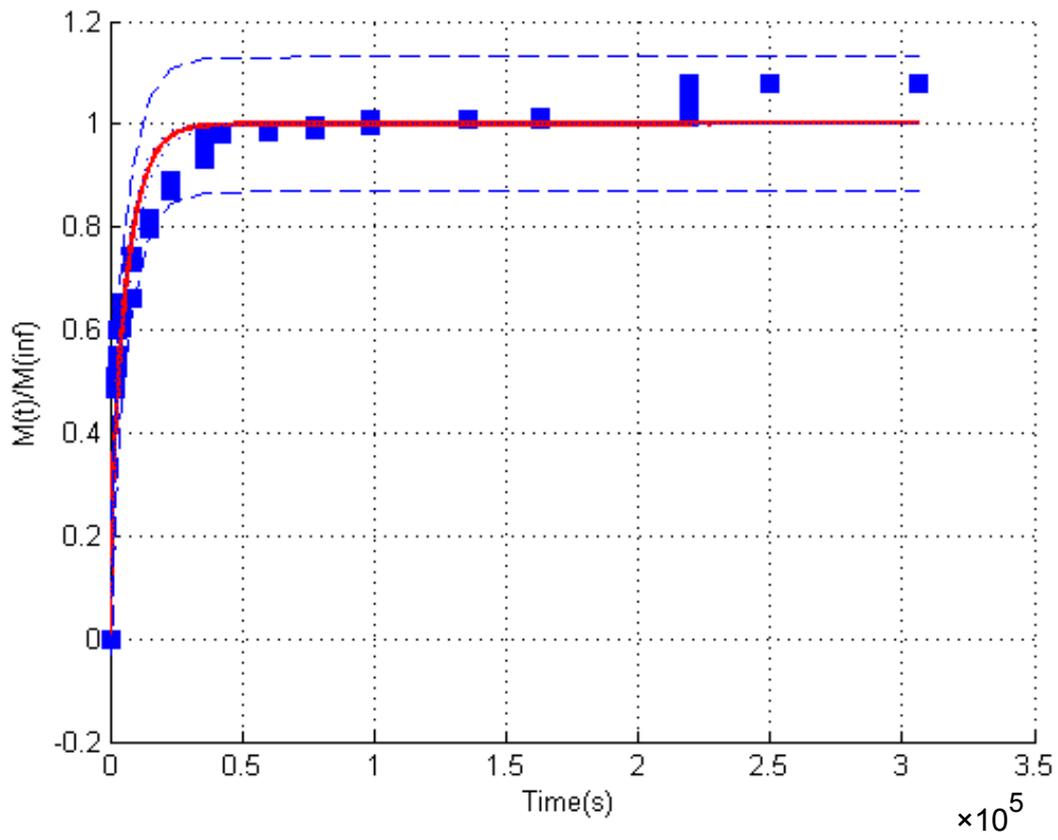
Figure 6.10 (cont'd)



T2R2-RES 23°C

(a)

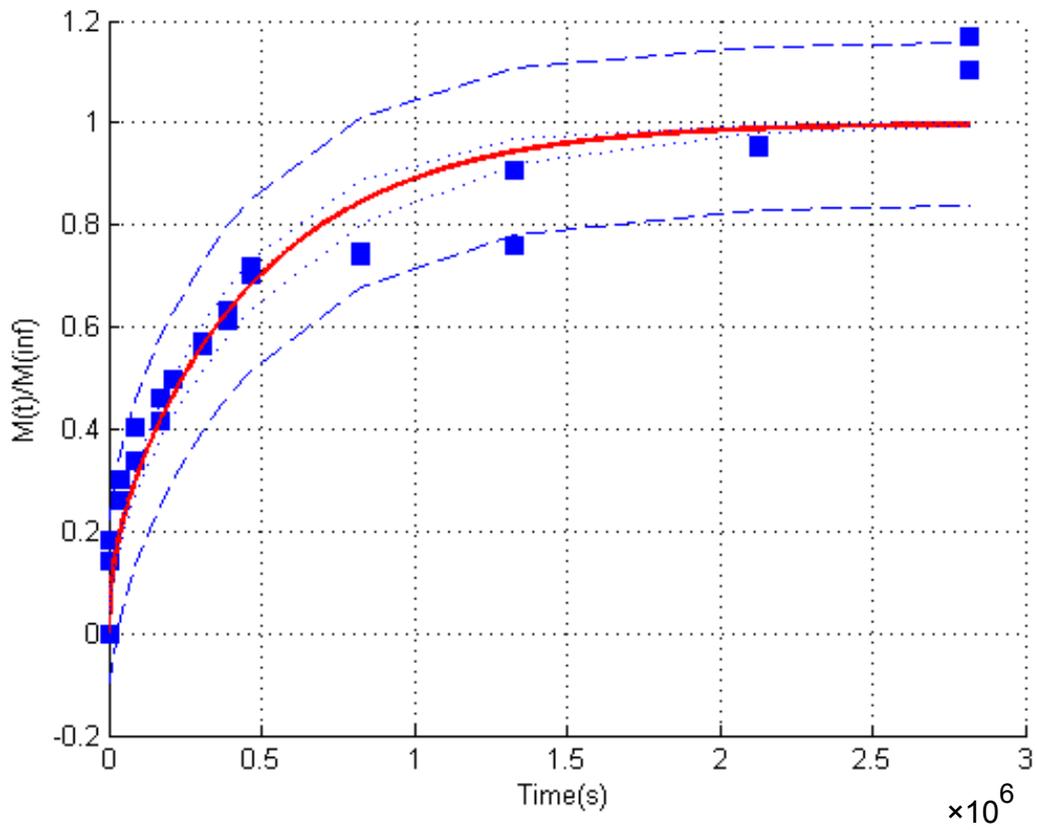
Figure 6.10 (cont'd)



T2R2-RES 43°C

(a)

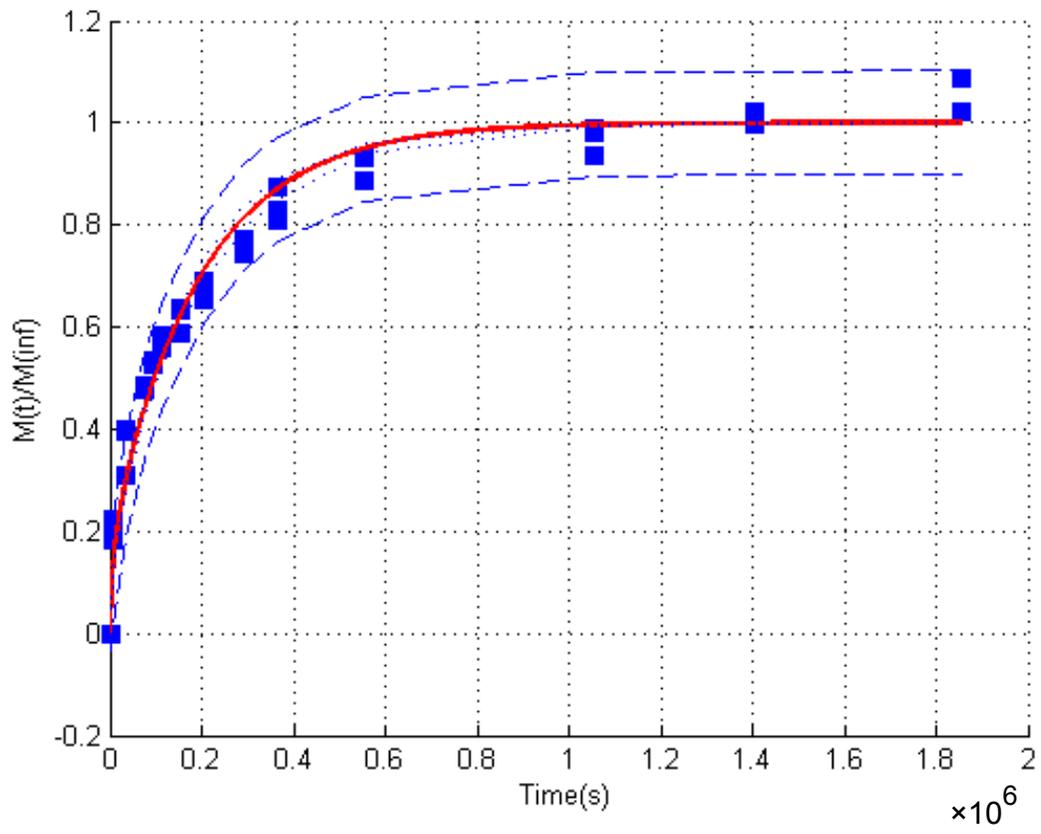
Figure 6.10 (cont'd)



T4R1-RES 13°C

(a)

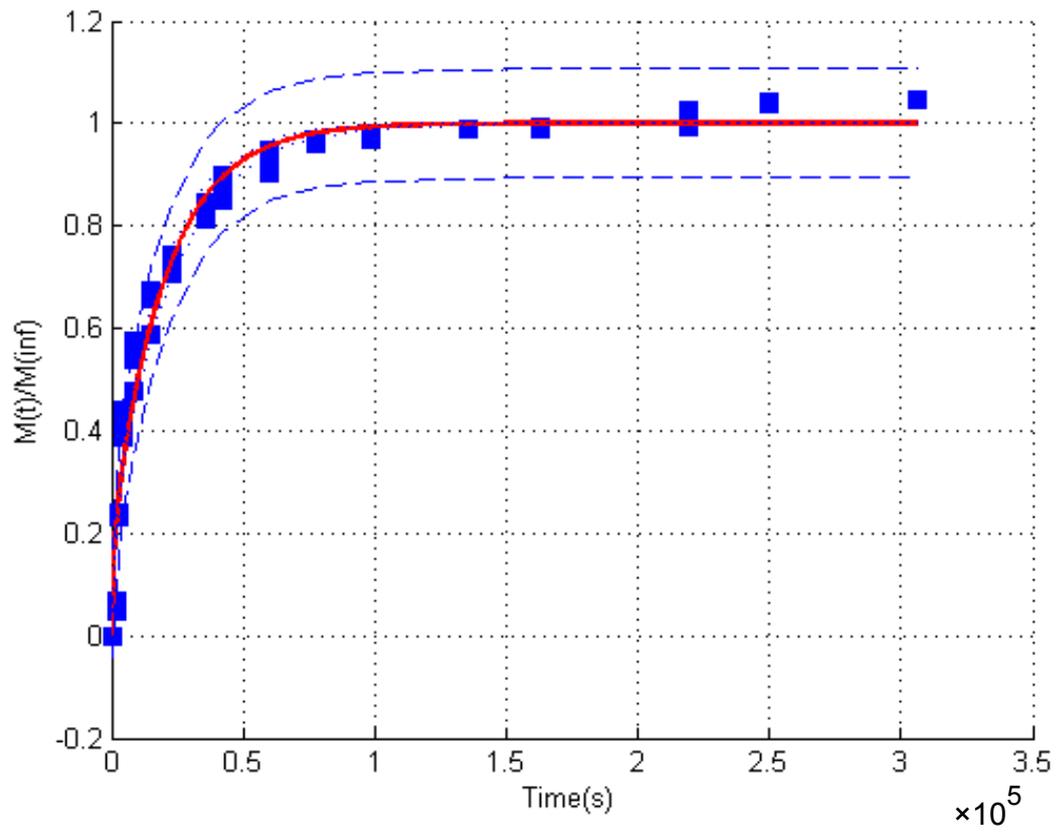
Figure 6.10 (cont'd)



T4R1-RES 23°C

(a)

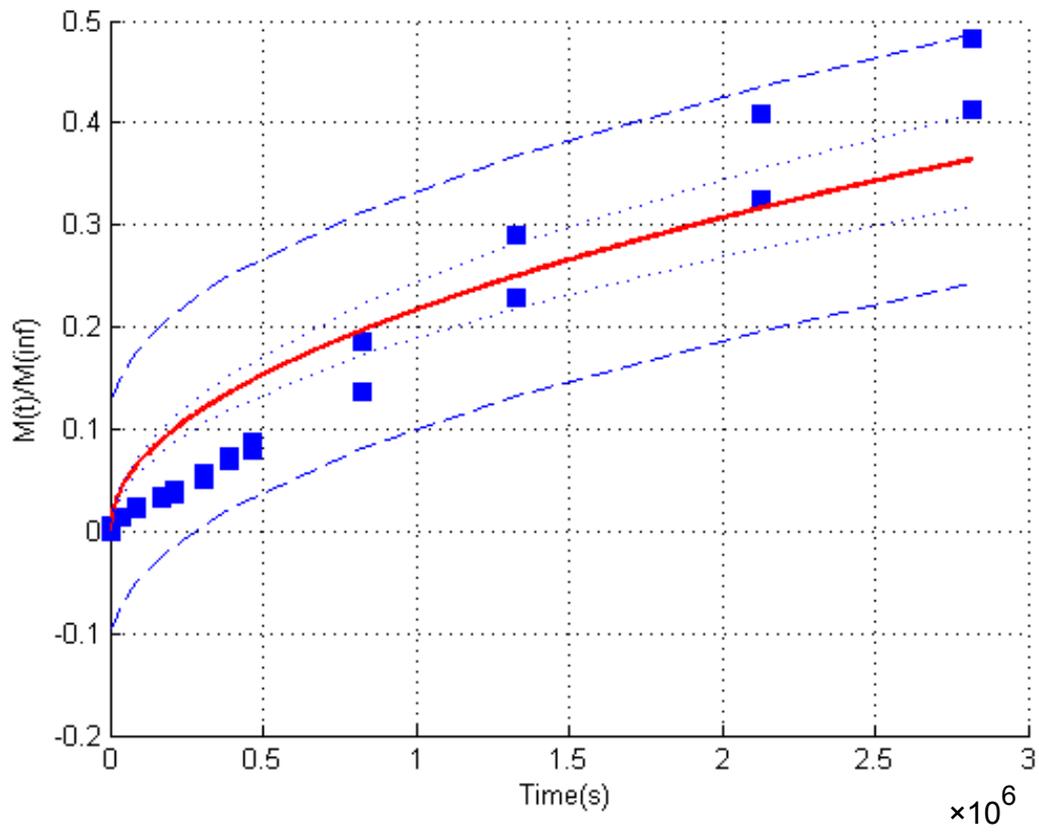
Figure 6.10 (cont'd)



T4R1-RES 43°C

(a)

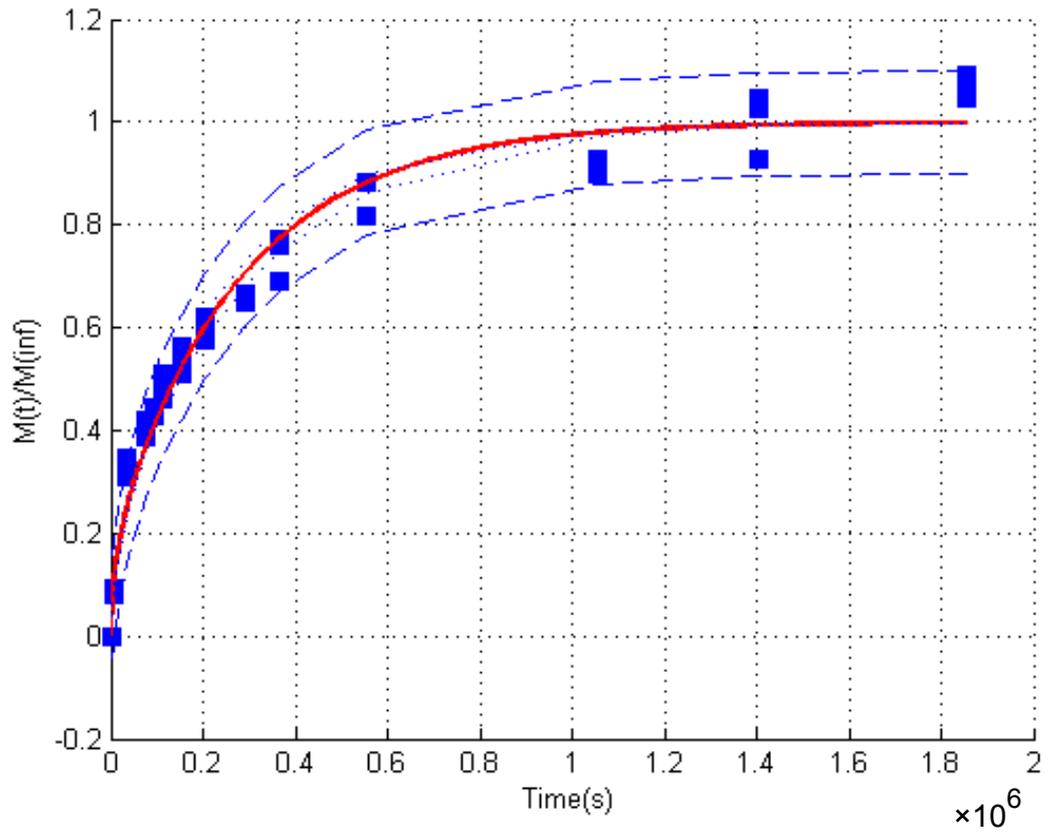
Figure 6.10 (cont'd)



T1R4-TOC 13°C

(b)

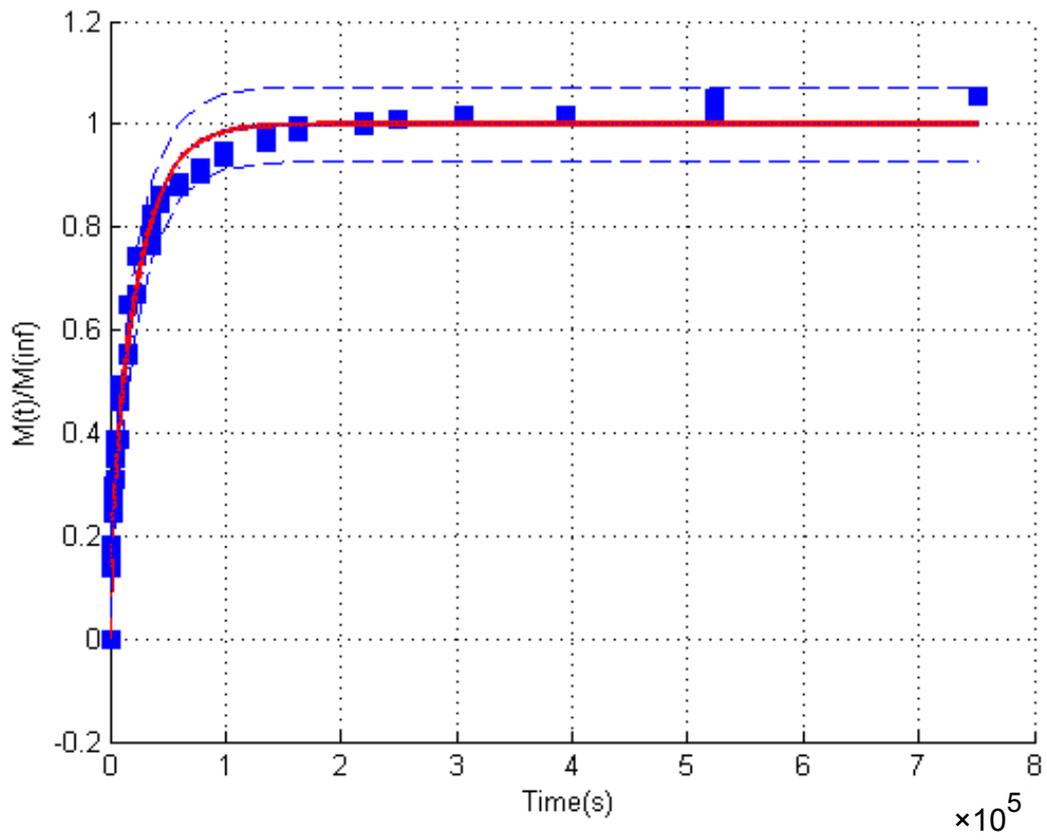
Figure 6.10 (cont'd)



T1R4-TOC 23°C

(b)

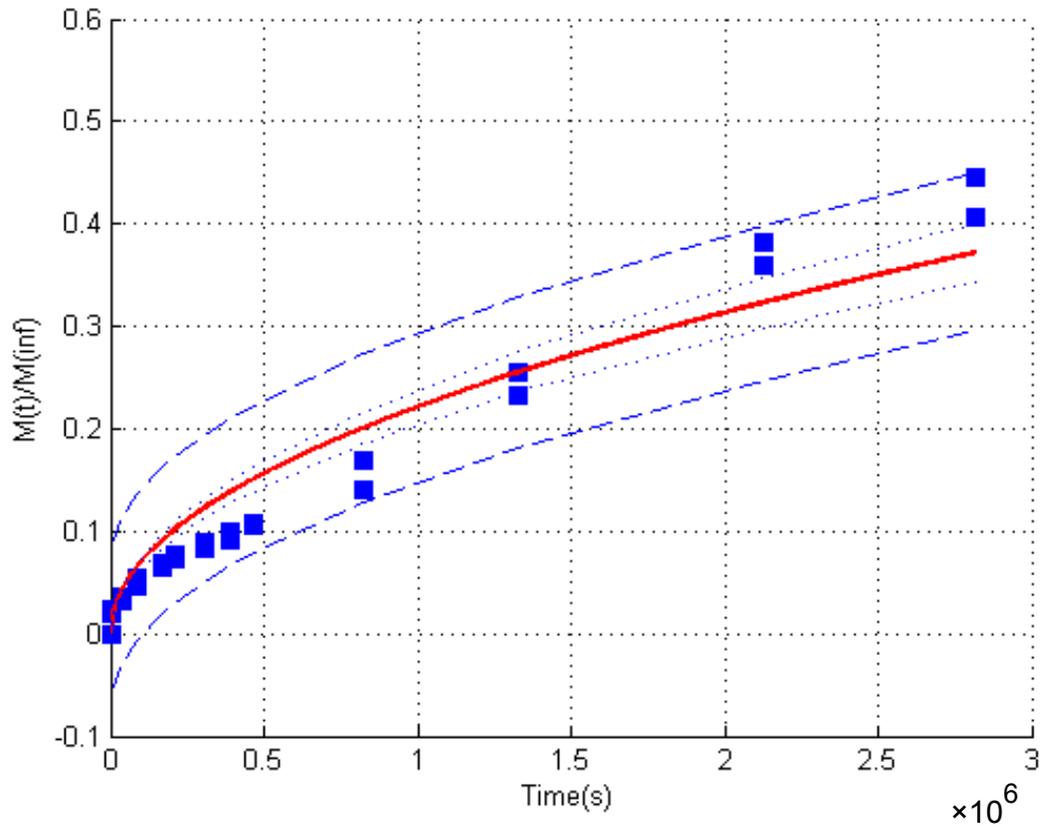
Figure 6.10 (cont'd)



T1R4-TOC 43°C

(b)

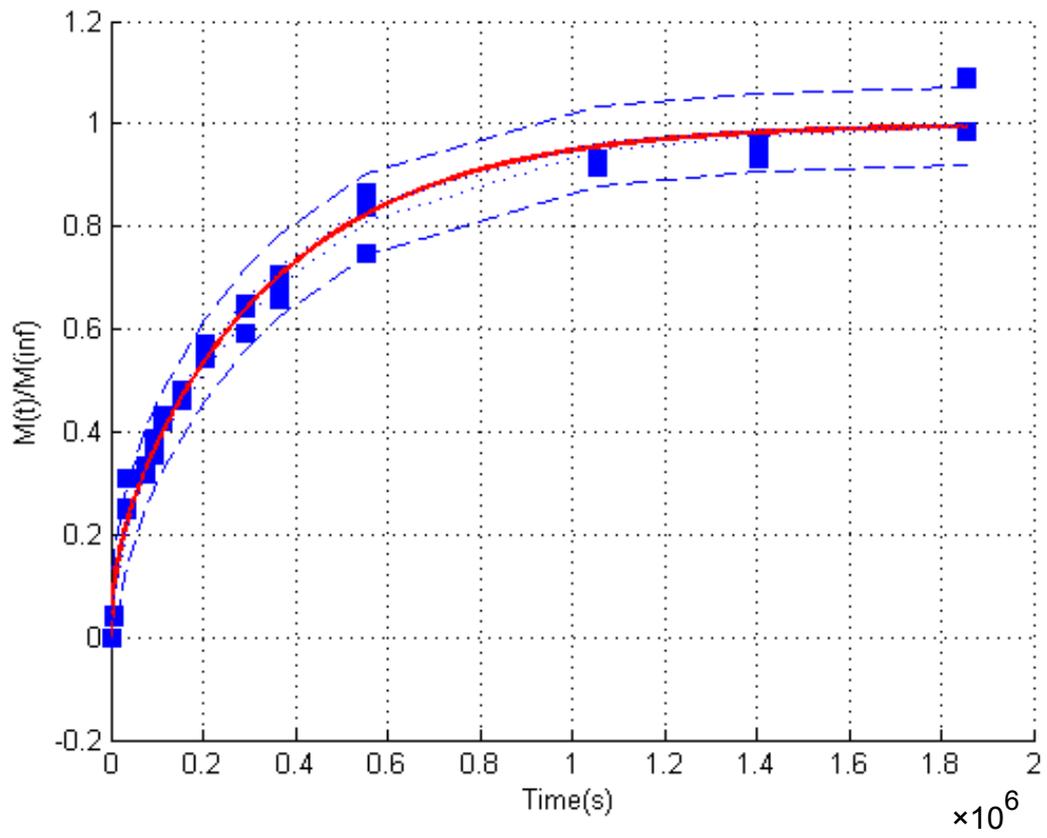
Figure 6.10 (cont'd)



T2R2-TOC 13°C

(b)

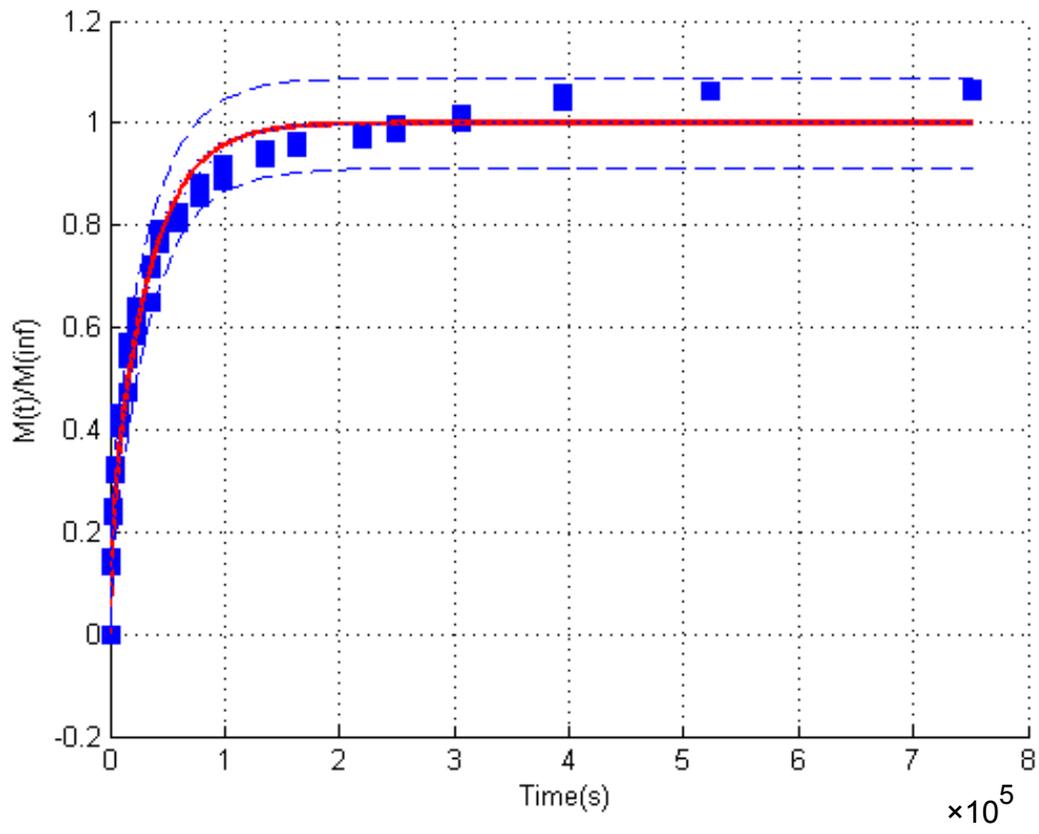
Figure 6.10 (cont'd)



T2R2-TOC 23°C

(b)

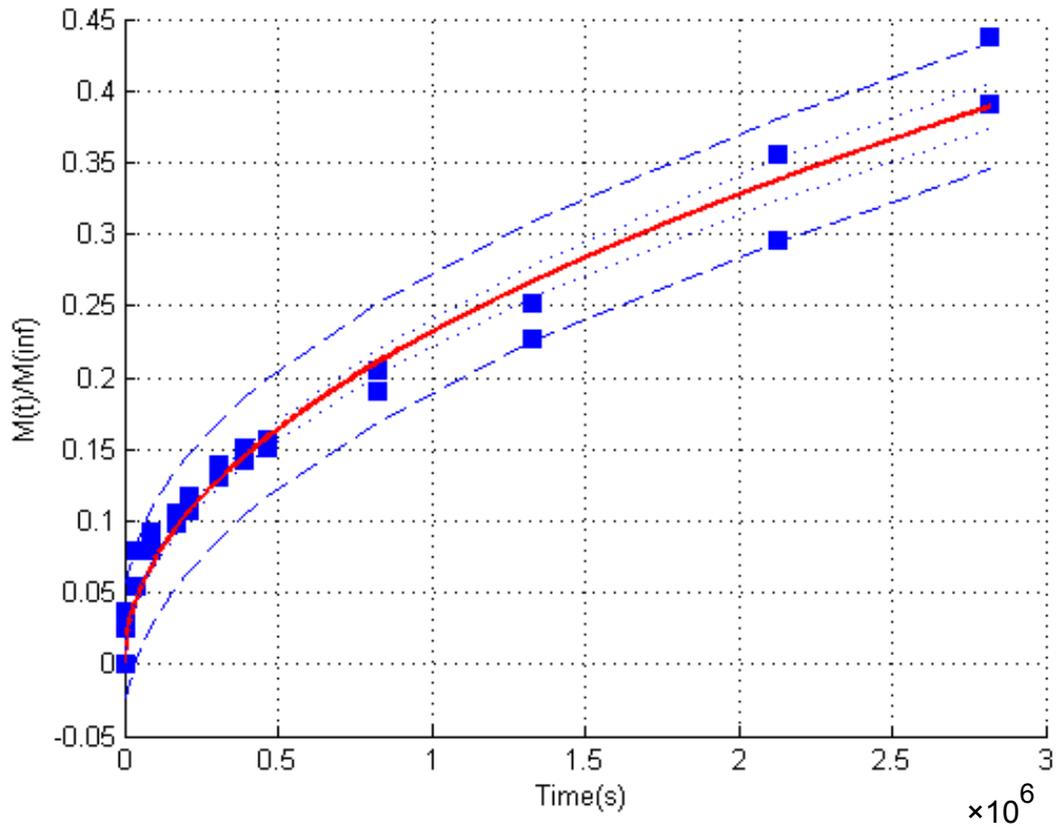
Figure 6.10 (cont'd)



T2R2-TOC 43°C

(b)

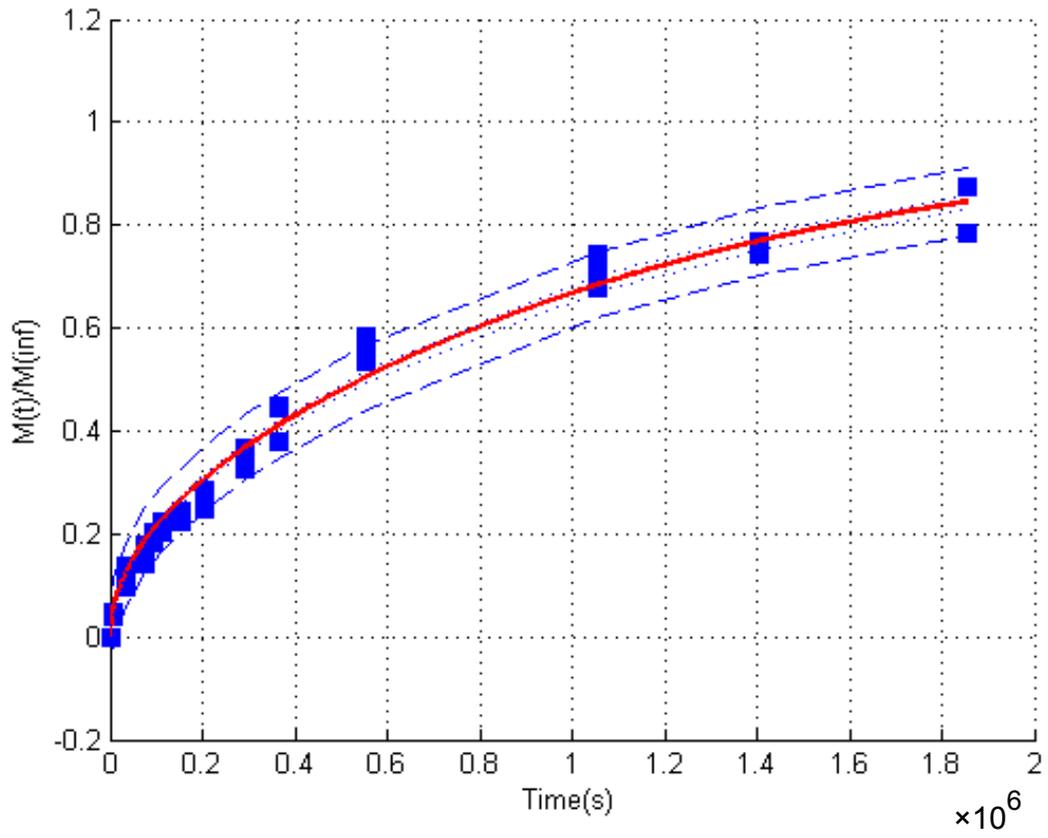
Figure 6.10 (cont'd)



T4R1-TOC 13°C

(b)

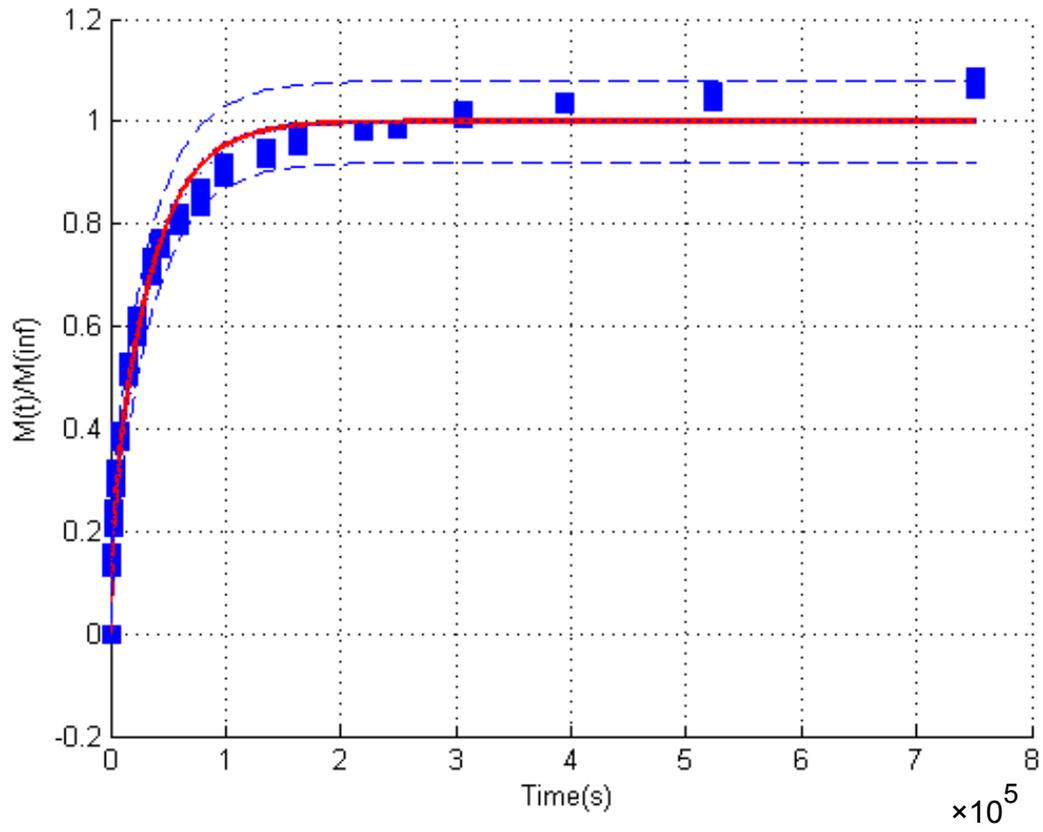
Figure 6.10 (cont'd)



T4R1-TOC 23°C

(b)

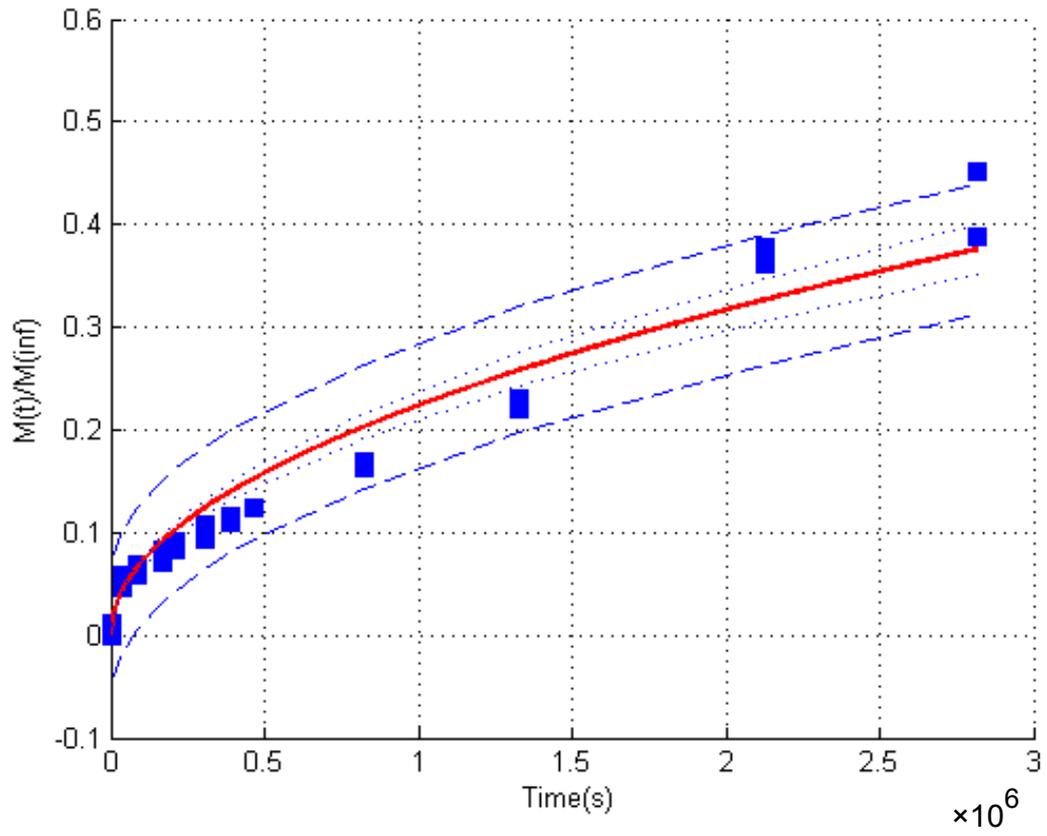
Figure 6.10 (cont'd)



T4R1-TOC 43°C

(b)

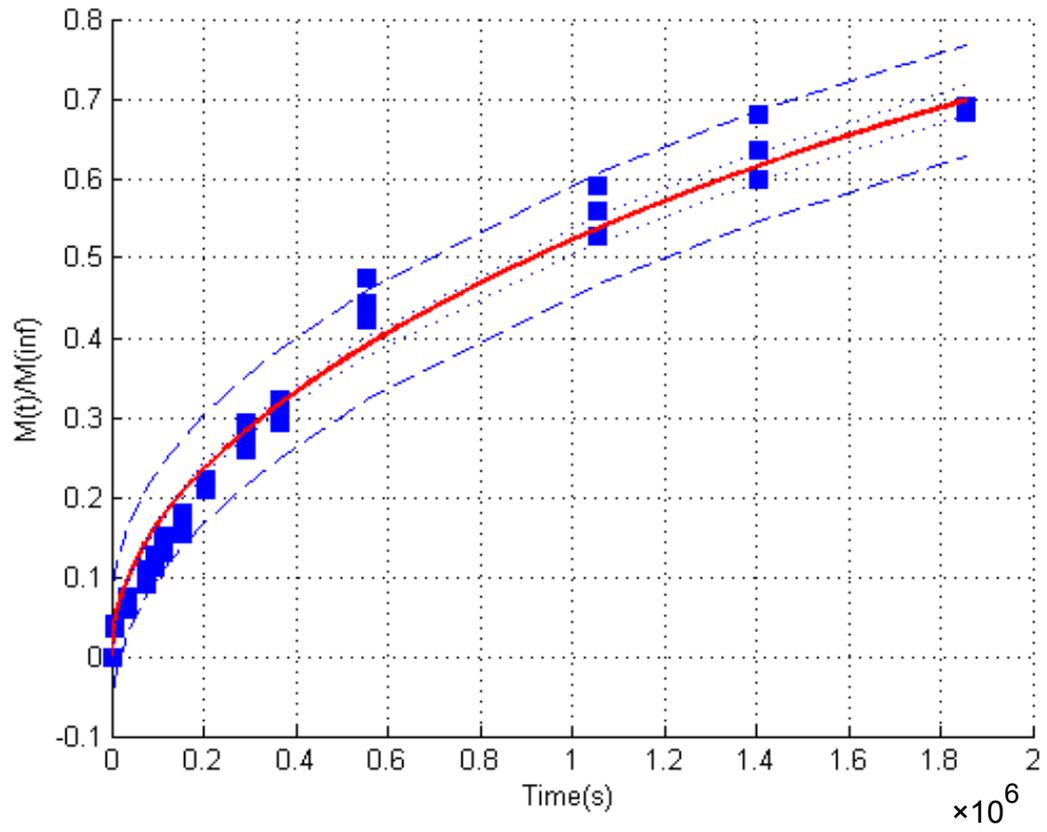
Figure 6.10 (cont'd)



T5R0-TOC 13°C

(b)

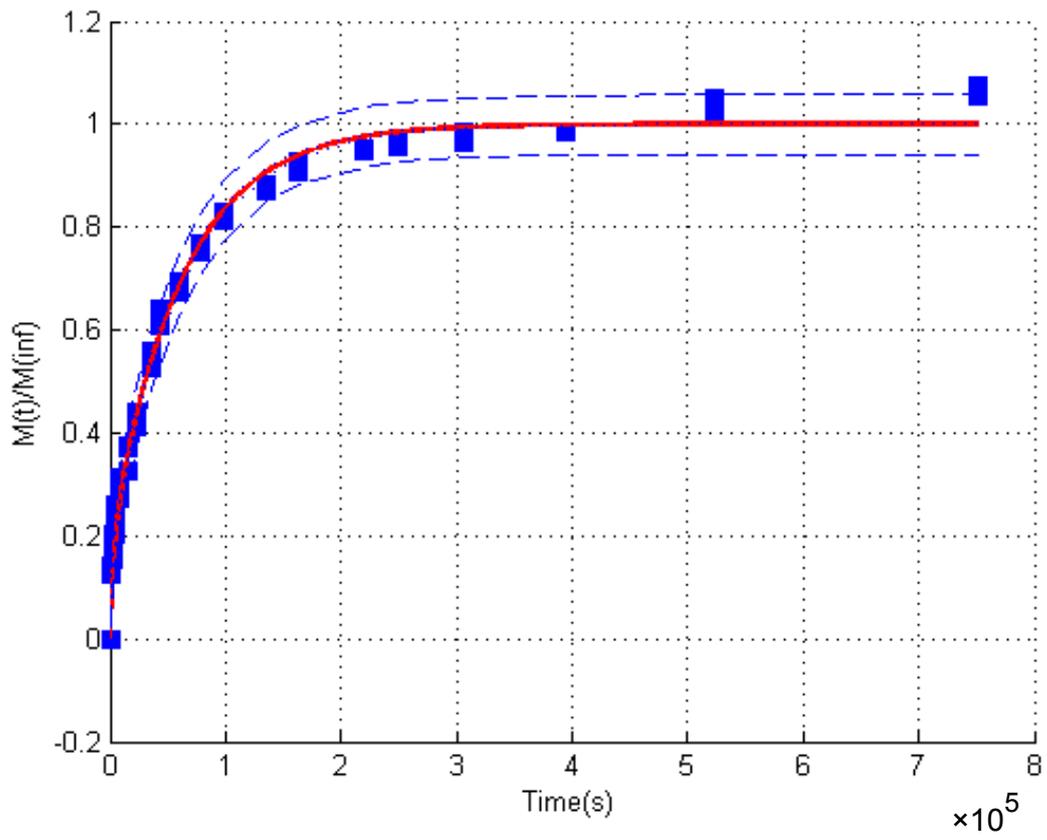
Figure 6.10 (cont'd)



T5R0-TOC 23°C

(b)

Figure 6.10 (cont'd)



T5R0-TOC 43°C

(b)

Diffusion coefficients (D) were estimated from Figure 6.9 a and b and 6.10 a and b according to Equation (5), and values are shown in Table 6.7 and 6.8. For resveratrol and α -TOC, the D values of all PLLA samples at 43 °C were one order of magnitude higher than the D values at 23 °C, which also were one order of magnitude higher than the D values at 13°C. Diffusion of resveratrol and α -TOC from PLLA/starch blends at 13, 23 and 43°C were at least one order of magnitude higher than the D values for PLLA films. The D values of α -TOC were found to be between $0.47 \sim 3.95 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA films and $0.70 \sim 6.83 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA/starch blend films at 13 °C, $5.67 \sim 13.0 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA films and $4.10 \sim 24.2 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA/starch blend films at 23 °C, and $89.0 \sim 118.0 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA films and $123 \sim 282 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA/starch blend films at 43 °C. The D values of resveratrol were found to be between $0.073 \sim 0.54 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA films and $1.42 \sim 6.93 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA/starch blend films at 13 °C, $0.90 \sim 3.44 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA films and $4.16 \sim 22.3 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA/starch blend films at 23 °C, and $24.8 \sim 74.1 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA films and $40.1 \sim 309 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA/starch blend films at 43 °C. The D values for resveratrol show a higher dependence on resveratrol concentration in PLLA and PLLA/starch blend films than the D values for α -TOC did for α -TOC concentration.

PLLA and PLLA/starch blend films with two antioxidants are new types of functional release membranes, so literature data was not available for one to one comparison.

Table 6.7 Diffusion Coefficient (D) of α -TOC from PLLA and PLLA/starch blend films into Ethanol at 13, 23, 43 °C

Sample	Parameter	Temperature, °C					
		13		23		43	
		PLLA	PLLA/Starch	PLLA	PLLA/Starch	PLLA	PLLA/Starch
T1R4	$D \times 10^{-11} (\text{cm}^2 \cdot \text{s}^{-1})$	0.47 ± 0.00^a	6.83 ± 0.05^a	5.67 ± 0.05^a	24.2 ± 0.5^a	104.3 ± 3.0^a	282 ± 4.0^a
	95% CI	(0.36, 0.59)	(6.08, 7.58)	(5.18, 6.15)	(22.3, 26.1)	(99.3, 109.2)	(264.4, 300.4)
	RMSE	0.0549	0.0504	0.0499	0.0495	0.0304	0.0365
T2R3	$D \times 10^{-11} (\text{cm}^2 \cdot \text{s}^{-1})$	0.78 ± 0.00^b	n/a	11.6 ± 0.4^b	n/a	96.7 ± 0.2^b	n/a
	95% CI	(0.66, 0.90)	n/a	(10.8, 12.4)	n/a	(93.5, 99.9)	n/a
	RMSE	0.0346	n/a	0.0395	n/a	0.0231	n/a
T2R2	$D \times 10^{-11} (\text{cm}^2 \cdot \text{s}^{-1})$	0.76 ± 0.00^b	4.63 ± 0.03^b	9.73 ± 0.03^c	22.2 ± 0.4^b	107.3 ± 3.0^a	239 ± 4.0^b
	95% CI	(0.69, 0.82)	(4.30, 4.95)	(9.30, 10.17)	(20.8, 23.6)	(101.8, 112.0)	(221.2, 256.1)
	RMSE	0.0197	0.0314	0.0263	0.0383	0.0295	0.0443
T3R2	$D \times 10^{-11} (\text{cm}^2 \cdot \text{s}^{-1})$	0.70 ± 0.00^b	n/a	13.0 ± 0.4^d	n/a	118.0 ± 3.0^c	n/a
	95% CI	(0.61, 0.79)	n/a	(12.2, 13.8)	n/a	(112.1, 124.4)	n/a
	RMSE	0.0287	n/a	0.0360	n/a	0.0341	n/a
T4R1	$D \times 10^{-11} (\text{cm}^2 \cdot \text{s}^{-1})$	3.95 ± 0.54^c	0.82 ± 0.00^c	9.40 ± 0.04^c	7.41 ± 0.03^c	89.0 ± 0.3^d	237 ± 4.0^b
	95% CI	(3.47, 4.43)	(0.72, 0.92)	(8.75, 10.06)	(7.01, 7.80)	(84.8, 93.1)	(221.4, 252.1)
	RMSE	0.0543	0.0282	0.0412	0.0308	0.0315	0.0395
T5R0	$D \times 10^{-11} (\text{cm}^2 \cdot \text{s}^{-1})$	n/a	0.70 ± 0.00^d	n/a	4.10 ± 0.03^d	n/a	123 ± 3.0^c
	95% CI	n/a	(0.58, 0.83)	n/a	(3.84, 4.37)	n/a	(117.9, 128.8)
	RMSE	n/a	0.0398	n/a	0.0332	n/a	0.0290

Values in the same column with different superscript letters were significantly different at $\alpha = 0.05$; All of the values are expressed as average values and standard error.

Table 6.8 Diffusion Coefficient (D) of Resveratrol from PLLA and PLLA/starch blend films into Ethanol at 13, 23, 43 °C

Sample	Parameter	Temperature, °C					
		13		23		43	
		PLLA	PLLA/Starch	PLLA	PLLA/Starch	PLLA	PLLA/Starch
T0R5	$D \times 10^{-10} (\text{cm}^2 \cdot \text{s}^{-1})$	n/a	6.93 ± 0.06^a	n/a	22.3 ± 0.4^a	n/a	309 ± 3.0^a
	95% CI	n/a	(5.88, 7.98)	n/a	(19.9, 24.9)	n/a	(284.9, 334.0)
	RMSE	n/a	0.0592	n/a	0.0443	n/a	0.0341
T1R4	$D \times 10^{-10} (\text{cm}^2 \cdot \text{s}^{-1})$	0.54 ± 0.00^a	4.16 ± 0.05^b	2.30 ± 0.03^a	16.5 ± 0.6^b	74.3 ± 0.4^a	263 ± 5.0^b
	95% CI	(0.49, 0.58)	(3.67, 4.64)	(2.20, 2.40)	(13.9, 19.1)	(68.1, 80.4)	(232.9, 293.6)
	RMSE	0.0411	0.0493	0.0274	0.0640	0.0393	0.0484
T2R3	$D \times 10^{-10} (\text{cm}^2 \cdot \text{s}^{-1})$	0.090 ± 0.00^b	n/a	3.44 ± 0.03^b	n/a	74.1 ± 0.4^a	n/a
	95% CI	(0.081, 0.098)	n/a	(3.29, 3.59)	n/a	(67.6, 80.5)	n/a
	RMSE	0.0234	n/a	0.0270	n/a	0.0435	n/a
T2R2	$D \times 10^{-10} (\text{cm}^2 \cdot \text{s}^{-1})$	0.073 ± 0.00^c	1.42 ± 0.12^c	2.14 ± 0.04^c	14.8 ± 0.7^c	55.6 ± 0.3^b	124 ± 6.0^c
	95% CI	(0.066, 0.080)	(1.04, 1.80)	(2.00, 2.27)	(12.5, 17.21)	(52.0, 59.2)	(106.7, 140.9)
	RMSE	0.0219	0.1238	0.0380	0.0741	0.0327	0.0649
T3R2	$D \times 10^{-10} (\text{cm}^2 \cdot \text{s}^{-1})$	0.073 ± 0.00^c	n/a	2.32 ± 0.03^a	n/a	48.4 ± 0.4^c	n/a
	95% CI	(0.066, 0.080)	n/a	(2.19, 2.45)	n/a	(45.1, 51.8)	n/a
	RMSE	0.0221	n/a	0.0340	n/a	0.0361	n/a
T4R1	$D \times 10^{-10} (\text{cm}^2 \cdot \text{s}^{-1})$	0.085 ± 0.00^b	1.66 ± 0.08^d	0.90 ± 0.03^d	4.16 ± 0.05^d	24.8 ± 0.3^d	40.1 ± 0.5^d
	95% CI	(0.079, 0.092)	(1.39, 1.94)	(0.85, 0.94)	(3.82, 4.50)	(23.6, 26.0)	(36.3, 44.0)
	RMSE	0.0182	0.0780	0.0302	0.0505	0.0286	0.0531

Values in the same column with different superscript letters were significantly different at $\alpha = 0.05$; All of the values are expressed as average values and standard error.

Therefore, comparison with films with one type of antioxidant was conducted. Soto *et al.* evaluated resveratrol diffusion from PLA films with 3 wt% of resveratrol into 100% ethanol and reported D values of 3.49×10^{-13} , 3.06×10^{-11} , 4.17×10^{-10} , and $8.26 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ at 9, 23, 33, and 43 °C, respectively[5]. The resveratrol D values in this study are one order of magnitude higher than in Soto-Valdez's study. Heirlings *et al.* studied D values for α -TOC from polymers such as LDPE and ethylene vinyl acetate copolymer (EVA) in 95% ethanol, and reported D values of 2.64×10^{-11} and $4.23 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$, respectively, at 7 °C[35]. Granda-Restrepo *et al.* reported D values of $2.34 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ for a multilayer film including an LDPE layer with 4 wt.% α -TOC in contact with whole milk powder at 20 °C[36]. Manzannarez-Lopez *et al.* recently prepared PLA films containing 2.58 wt.% of α -TOC, and evaluated the kinetics of release of α -TOC from the PLLA films to ethanol at temperatures between 23 and 43 °C. D values of 3.16×10^{-11} , 5.29×10^{-11} , and $38.0 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ at 23, 33, and 43 °C, respectively, were reported. The D value for α -TOC in this study also showed same or one order of magnitude higher value. From this study, migration from the dual antioxidant system appears to be faster than that from single systems. The D value for resveratrol is higher than that for α -TOC due to its small molecular size giving higher mobility. In addition, although the improved interfacial adhesion between PLLA/starch blends was found in our previous study[23], the morphological instability of interfacial region in PLLA/starch blends could result in much higher D values as compared to PLA-resveratrol and PLA- α -TOC single system. The chain softening at 43 °C, which is near the T_g of PLLA, could accelerate the diffusion of resveratrol and α -TOC from PLLA and PLLA/starch blend films as well.

6.3.8. Activation energy of diffusion (E_a) α -TOC and resveratrol for PLLA and PLLA/starch blend films into ethanol

A plot of $\ln(D)$ vs. T^{-1} for resveratrol and α -TOC (Figure 6.11 a and b) produced a straight line for all PLLA ($R^2 = 0.9597 \sim 0.9955$) and PLLA/starch blend samples ($R^2 = 0.9627 \sim 0.9993$)

For resveratrol, the PLLA films had an E_a of 132.6 ± 0.1 , 116.3 ± 0.4 , 120.4 ± 0.4 , 123.5 ± 0.4 , and 79.2 ± 0.1 $\text{kJ}\cdot\text{mol}^{-1}$ for T1R4, T2R3, T2R2, T3R2, and T4R1, respectively, and E_a values of

125.1 ± 0.2 , 162.5 ± 0.3 , 161.8 ± 0.3 , 157.5 ± 0.4 and 140.6 ± 0.1 $\text{kJ}\cdot\text{mol}^{-1}$ for T1R4, T2R3,

T2R2, T3R2, and T4R1 $\text{kJ}\cdot\text{mol}^{-1}$, respectively, were found for α -TOC. For PLLA/starch blend

films, for resveratrol the E_a of 96.2 ± 0.1 , 104.5 ± 0.0 , 108.5 ± 0.3 , and 80.8 ± 0.1 $\text{kJ}\cdot\text{mol}^{-1}$ was

found for T0R5, T1R4, T2R2, and T4R1, respectively, and E_a of T1R4, T2R2, T4R1, and T5R0

$\text{kJ}\cdot\text{mol}^{-1}$ for α -TOC was found to be 92.4 ± 0.0 , 96.0 ± 0.1 , 135.8 ± 0.1 , and 121.4 ± 0.0 $\text{kJ}\cdot\text{mol}^{-1}$,

respectively ($R^2 = 0.8628 \sim 0.9971$) (see Table 6.9). The E_a values for resveratrol obtained

from both PLLA and PLLA/starch blend were lower than the reported value for PLA-resveratrol (176 $\text{kJ}\cdot\text{mol}^{-1}$) while the E_a of α -TOC for PLLA and PLLA/starch blend films were higher than

reported values from PLA- α -TOC (96.2 $\text{kJ}\cdot\text{mol}^{-1}$) except for T4R1 and T5R0[4, 5]. It was

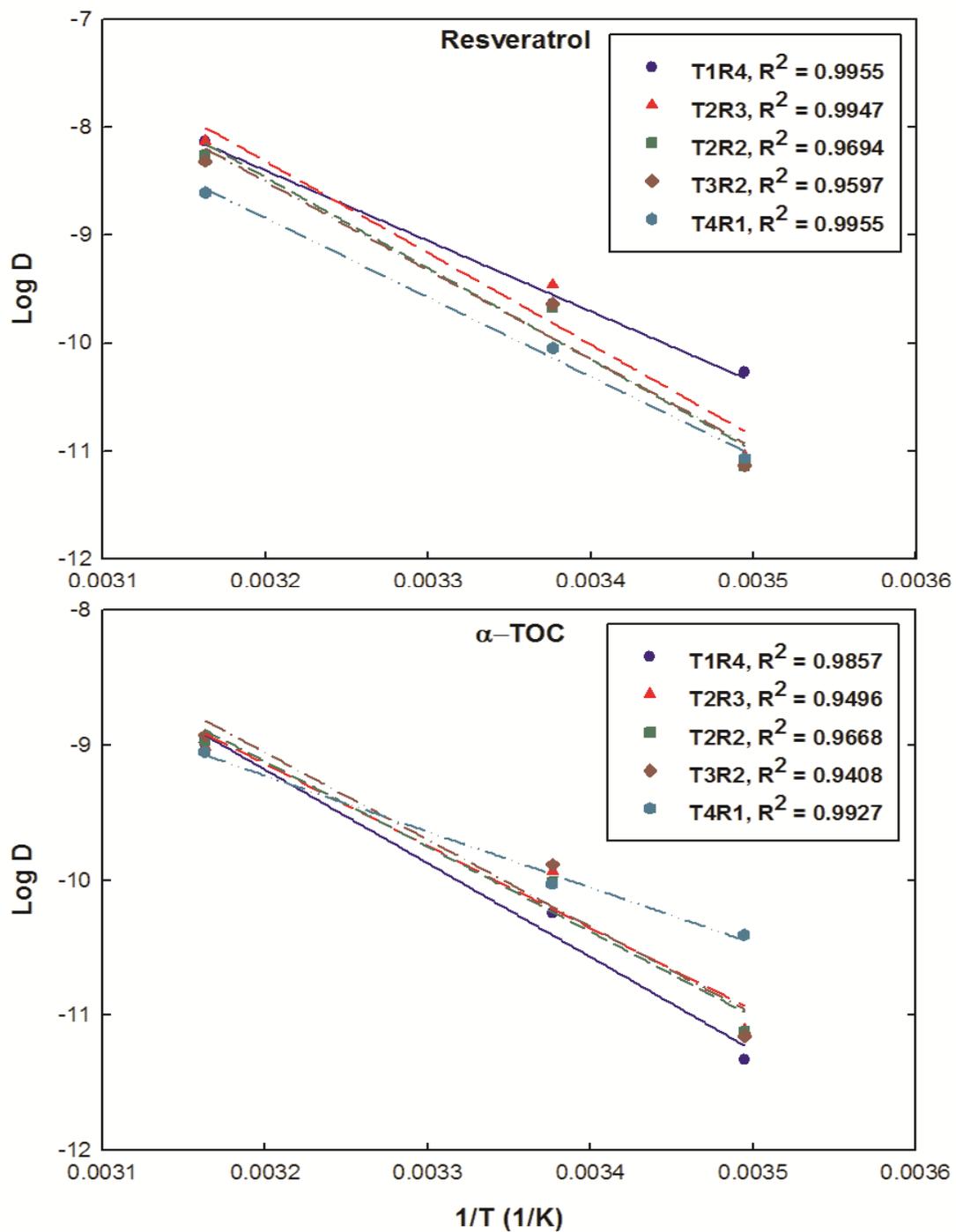
reported that less energy is needed for diffusion of α -TOC from PLA to ethanol compared to

diffusion of resveratrol since resveratrol has two aromatic rings and three hydroxyl groups,

allowing the molecule to interact with the polar groups in PLLA and thus requiring more energy

to diffuse among the PLA chains[4]. Thus, α -TOC required much higher energy to diffuse from

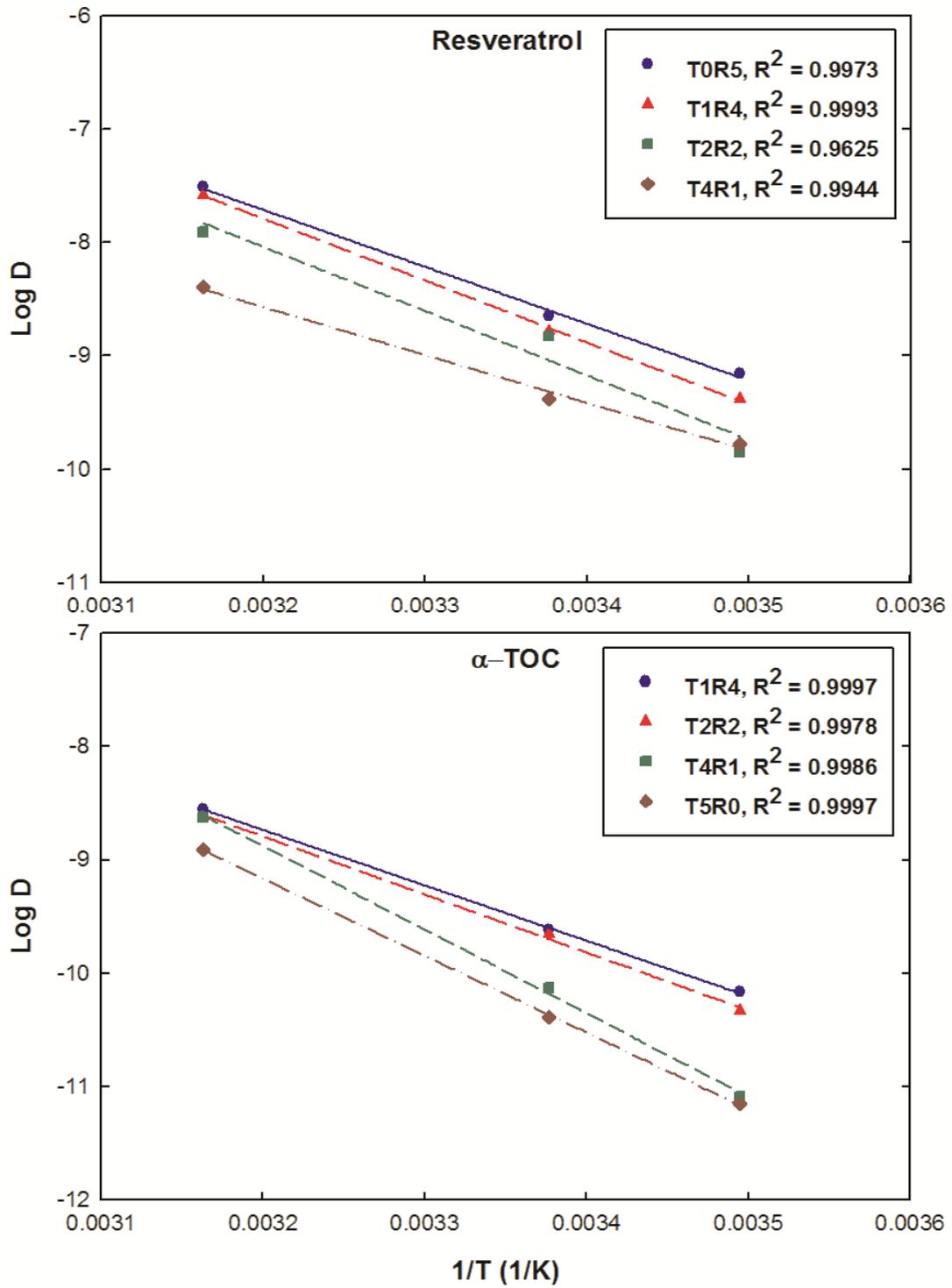
PLLA in the presence of resveratrol as compared to when it is alone. This can be attributed to coexistence of two antioxidants, α -TOC and resveratrol, having molecular interaction within PLLA and PLLA/starch blend resulting in restriction of molecule movements among them. Even lower energy was required for PLLA/starch blend as compared to PLLA films. MAH was used as a compatibilizer between PLLA and starch, reacting with the hydroxyl groups of PLLA and starch to improve the interfacial adhesion of the PLLA/starch blend. This high interaction between MAH and hydroxyl group of PLLA and starch would give less chance for resveratrol to have the molecular interaction with PLLA and starch resulting in the lower E_a .



(a) PLLA

Figure 6.11. The activation energy of the diffusion of resveratrol and α -TOC from PLLA (a) and PLLA/starch blend films (b) to ethanol, and the slope of each line was equal to $-E_a/2.303R$

Figure 6.11 (cont'd)



(b) PLLA/starch blend

Table 6.9. Activation energy of the diffusion (E_a) of resveratrol and α -TOC into Ethanol from PLLA and PLLA/starch blend films

Sample	Activation Energy, $\text{kJ}\cdot\text{mol}^{-1}$			
	PLLA		PLLA/starch	
Antioxidant	α -TOC	Resveratrol	α -TOC	Resveratrol
T0R5	n/a	n/a	n/a	96.2 ± 0.1^a
T1R4	125.1 ± 0.2^a	132.6 ± 0.1^a	92.4 ± 0.0^a	104.5 ± 0.0^b
T2R3	162.5 ± 0.3^b	116.3 ± 0.4^b	n/a	n/a
T2R2	161.8 ± 0.3^b	120.4 ± 0.4^c	96.0 ± 0.1^b	108.5 ± 0.3^c
T3R2	157.5 ± 0.4^c	123.5 ± 0.4^d	n/a	n/a
T4R1	140.6 ± 0.1^d	79.2 ± 0.1^e	135.8 ± 0.1^c	80.8 ± 0.1^d
T5R0	n/a	n/a	121.4 ± 0.0^d	n/a

Values in the same column with different superscript letters were significantly different at $\alpha = 0.05$; All of the values are expressed as average values and standard error.

6.4. Conclusions

PLLA and PLLA/starch blend films with added α -TOC and resveratrol were produced. The T_g and T_m of the PLLA/starch blend films were significantly reduced with the addition of antioxidants, while the thermal stability was improved. The enhanced mechanical properties can be attributed to not only a compatibilization effect based on the chemical linkage between PLLA and starch chains, but also to restriction of the chain mobility by the antioxidants. The release of resveratrol from PLLA and PLLA/starch blend films into ethanol followed Fickian behavior. The D values of α -TOC were found to be between $0.47 \sim 3.95 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA films and $0.70 \sim 6.83 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA/starch blend films at 13°C , $5.67 \sim 13.0 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$

for PLLA films and $4.10 \sim 24.2 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA/starch blend films at 23 °C, and $89.0 \sim 118.0 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA films and $123 \sim 282 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA/starch blend films at 43 °C. The D values of resveratrol were found to be between $0.073 \sim 0.54 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA films and $1.42 \sim 6.93 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA/starch blend films at 13 °C, $0.90 \sim 3.44 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA films and $4.16 \sim 22.3 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA/starch blend films at 23 °C, and $24.8 \sim 74.1 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA films and $40.1 \sim 309 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA/starch blend films at 43 °C. Release of antioxidants from PLLA and PLLA/starch blends with dual antioxidant systems differed from that of PLLA with a single antioxidant. Morphological instability such as cavities can result in higher D values and the molecular interaction between the antioxidants and the polymers can have a critical effect on in the values of D and E_a in PLLA and PLLA/starch blend systems.

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CHAPTER VII

CHAPTER VII

Conclusions and Future Work

7.1 General conclusions

The objective of this research was to develop PLLA and PLLA/starch blends containing two antioxidants, α -TOC and resveratrol, as active functional membranes for food and pharmaceutical packaging systems. This thesis describe a methodology to produce PLLA and PLLA/starch blend films added with α -TOC and resveratrol at different concentration levels. The effect of the addition of these two natural antioxidants on the optical, physical, thermal, and mechanical properties of PLLA and PLLA/starch blend films were assessed. Furthermore, this work also addresses the release kinetics of α -TOC and resveratrol from PLLA/antioxidant and PLLA/starch/antioxidant blend films into a food stimulant, ethanol, at three different temperatures (13, 23, and 43 °C).

In the first phase, PLLA films containing two natural antioxidants, α -TOC and resveratrol with various concentrations, were fabricated by melt compounding and compression molding processes. The influence of the antioxidants on the optical, color and UV-VIS light transmission, and thermal properties was analyzed. The mechanical, thermo-mechanical and rheological properties of the films were also assessed. It was noted that the addition of α -TOC and resveratrol increased the a^* (redness) and b^* (yellowness) values of the PLLA/antioxidant films. These samples showed slightly more hydrophobic characteristics than neat PLLA films due to the energy dispersive component. Increase in the elastic modulus with varying concentrations of the two antioxidants was found in PLLA/antioxidant films. The combination of α -TOC and resveratrol affected on $\%T$, T_g and X_c . Both antioxidants affected the mechanical and thermo-

mechanical properties of PLLA films. The melt viscosity of the PLLA/antioxidant films was substantially higher than that of neat PLLA. The $G'(\omega)$ of the PLLA/antioxidant films was found to be higher than that of neat PLLA films over the entire frequency range. These higher melt viscosity and $G'(\omega)$ values could be an indication of formation of entanglements between PLLA and α -TOC and resveratrol. These results show potential feasibility for using PLLA/antioxidant films as active functional membranes for food, pharmaceutical, and medical packaging applications.

In the second phase, the MAH was grafted onto PLLA, PLLA-g-MAH, in the presence of DCP as an initiator, and the dependence of the MAH grafting reaction onto PLA on the concentration of DCP and MAH was investigated. The thermal and mechanical properties were assessed to determine the optimized concentration of DCP and MAH as a potential compatibilizer for PLLA blends. Grafting of MAH onto PLLA was successfully achieved and confirmed by both FT-IR and $^1\text{H-NMR}$. Introduction of a small amount of MAH greatly reduced gel content by increasing the grafting yield. The T_g and $\% X_c$ were significantly decreased by the addition of MAH due to chain branching resulting from the grafting reaction between PLLA and MAH and the resultant increase in the segmental mobility of the PLLA chain. Reduced thermal stability of the maleated PLLA as compared to neat PLLA was found, correlating with the molecular weight decrease of the PLLA-g-MAH samples. The thermal stability of the samples was influenced by the MAH content while the mechanical properties were not affected much by the grafting reactions.

In the third phase, the research focused on the production of PLLA/starch blends with different compositions of PLLA and starch. The thermal, thermo-mechanical, mechanical, and morphological properties were evaluated to assess the compatibility of the PLLA/starch blends.

It was found that the MAH acted as a good compatibilizer for the PLLA and starch blends in the presence of DCP as an initiator. T_g and T_m decreased with reactive compatibilization; however, the thermo-mechanical properties of PLLA/starch with reactive compatibilization were significantly improved as compared to blends without reactive compatibilization. PLLA/starch (80/20) blend with 2.0 phr of MAH and 0.1 phr of DCP had an E' of 3.9 GPa at 40°C, and tensile strength of 51.7 MPa at 23°C, and elongation at break of 3.3 %, which were close to neat PLLA. Enhanced interfacial adhesion between PLLA and starch was observed due to the compatibilization effect of MAH grafted onto PLLA and starch. Reactive compatibilization significantly reduced the combined molecular weight of PLLA/starch blends.

In the final phase, PLLA/starch blend films with added α -TOC and resveratrol were produced. It was found that the T_g and T_m were significantly reduced with the addition of antioxidants, while the thermal stability was improved. The enhanced mechanical properties could be attributed to not only a compatibilization effect based on the chemical linkage between PLLA and starch chains, but also restriction of the chain mobility by the antioxidants. The release of resveratrol from PLLA and PLLA/starch blend films into ethanol followed Fickian behavior. The D values of α -TOC were found to be between $0.47 \sim 3.95 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA films and $0.70 \sim 6.83 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA/starch blend films at 13 °C, $5.67 \sim 13.0 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA films and $4.10 \sim 24.2 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA/starch blend films at 23 °C, and $89.0 \sim 118.0 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA films and $123 \sim 282 \times 10^{-11} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA/starch blend films at 43 °C. The D values of resveratrol were found to be between $0.073 \sim 0.54 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA films and $1.42 \sim 6.93 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA/starch blend

films at 13 °C, $0.90 \sim 3.44 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA films and $4.16 \sim 22.3 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA/starch blend films at 23 °C, and $24.8 \sim 74.1 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA films and $40.1 \sim 309 \times 10^{-10} \text{ cm}^2 \cdot \text{s}^{-1}$ for PLLA/starch blend films at 43 °C. The release behavior for PLLA and PLLA/starch blends with dual antioxidants differed from that of PLLA with a single antioxidant. The morphological instability could result in higher D values and the molecular interaction between the antioxidants and the polymers could have a critical effect on determining in D and E_a in PLLA and PLLA/starch blend systems. Overall, the studies showed that there is potential feasibility of PLLA or PLLA/starch blend packaging systems with single and dual antioxidants as active functional membranes for oxygen sensitive food or pharmaceutical products.

7.2 Recommended future work

In future work it would be useful to examine the micro-scale structure of PLLA and PLLA/starch blends with two antioxidants to understand the physical/chemical interactions among PLLA, starch and the antioxidants. In addition, it would be valuable to apply PLLA and PLLA/starch blend films with α -TOC and resveratrol in antioxidant active packaging systems with real food and/or pharmaceutical products to determine the effect of the antioxidant release on the oxidative stability of those products and determine whether it results in enhanced shelf life of the products.

Multilayer film structures are commonly used in food and pharmaceutical packaging applications; however, there has been little investigation of the release behavior of antioxidants from multilayer film structures composed of bio-based materials. In alternating multilayer film structures, the concentration profile of antioxidant would be different; therefore, different release

behavior would be expected due to concentration profile. This would lead to future work in the development of multilayer antioxidant packaging films.