POLYLACTIC ACID: A POTENTIAL SUSTAINABLE BIO-BASED
CONTROLLED RELEASE PACKAGING POLYMER

by

SAIFANASSOUR ALI ARABI

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And approved by

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ABSTRACT OF THE DISSERTATION

Polylactic acid: a potential sustainable bio-based controlled release packaging polymer

By SAIFANASSOUR ALI ARABI

Dissertation Director:

Professor Kit L. Yam

Polylactic acid (PLA), a bio-based polymer produced from fermentation of starch into lactic acid followed by polymerization process, is considered to be a sustainable packaging material. Stereochemical isomers, P-LLA and P-DLA, affect polymer final properties and can be used in controlled release packaging (CRP) to provide a wide range of release profile. CRP is a new generation of functional packaging materials in which the package acts as a delivery system for antimicrobials or antioxidants. The delivery occurs in a timely manner to increase shelf life and maintain safety and quality of the food.

This study is divided into two parts. The first part aimed at investigating the effects of stereochemical isomers and processing conditions (drying and annealing) on release
profile of tocopherol and film properties. The second part investigated the effect of two processing methods, solvent and extrusion casting, on tocopherol release kinetics and film properties.

PLA containing different ratios of stereochemical isomers was impregnated with 3000ppm tocopherol using solvent casting and commercial scale extrusion casting methods to produce the films. The solution casting films were first dried at room temperature for 24 hours and further dried at 40°C. The films from both methods were annealed at 120°C for 4 hours. Then release study was conducted to monitor the release of tocopherol over time on the annealed and unannealed films.

Results of the first part showed varied tocopherol release profiles and diffusivities (2.42X10^{-19} to 8.68X10^{-16} m^2/s) with three orders of magnitude. Annealing process increased film crystallinity, which led to lower diffusivity and slower tocopherol release. It also decreased water vapor and oxygen transmission rates of the films. Results of the second part showed that solvent casting and extruded films had different tocopherol release profiles but shared similar trend. Scanning electron microscopy performed on films from two methods revealed different topographies. The films from both methods were only comparable in terms of mechanical properties such as tensile strength.

Overall, results suggest that while a wide range of tocopherol release profile using solvent casting method is achievable; data from solvent casting cannot extrapolate directly to extrusion casting in terms of tocopherol release profile.
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1 INTRODUCTION

Shelf life of food is defined by Lee et al as “the period of time during which a food retains acceptable characteristics of flavor, color, aroma, texture, nutritional value, and safety under defined environmental conditions.” [2]. This statement is one of the most descriptive definitions related to shelf life and implies the crucial role of packaging in the process of food quality, safety, and shelf life extension. Packaging of food is not as straightforward as an ordinary end user might think; it is a synchronized system of science and art that can be seen in the basic functions of food packaging which are protection, convenience, communication, and containment [2]. The innovations in food packaging technology is not driven only by these four functions but also driven by the prediction of storage life for different type of food such as fresh and semi-processed foods and whether for civilian (during crises or normal life), military (different war zones), or astronauts (space travel). Scientists in the area of packaging science & technology and polymer science have established different type of packaging technologies such as modified atmosphere packaging (MAP), vacuumed packaging (VP), controlled release packaging (CRP) which include antimicrobial and antioxidant packaging, etc., to address the issues related to food quality retention and shelf life extension from farmer through retailer to consumer [3]. The new packaging technology system is emphasis the basic four functions of food packaging.
Among all above-mentioned packaging technologies as means of extending food shelf life, CRP has gain more interest in the recent years. CRP represents a new generation of functional packaging materials in which the package acts as a delivery system for active compounds (AC) such as antimicrobials and antioxidants. The active compound (AC) is released in a timely manner to enhance safety, retain quality, and extend shelf life of food [4].

The application of CRP has been widely and effectively used in pharmaceuticals and drug industries, in different forms and diverse release rates, for quite sometimes [5-17] while its application in food industry is relatively new. An example of a CRP application in food which is already exists in the market is the use of BHT as antioxidant to extend the shelf life of breakfast cereal [18].

Designing a CRP for food application is interesting but at the same time is very challenging, especially when the release profile of active compounds incorporated depends on the polymer type, structures, and morphology. These parameters determine the release rate or profile, besides the size of active compounds and storage temperature [4]. The ultimate concept of CRP is to manipulate polymer morphology to achieve the required release kinetics (fast or slow release) to match the food type. In case of release profile of active compounds from synthetic polymers e.g. polypropylene (PP) and high density polyethylene (HDPE) individually, the release is set to one profile either slow or fast, and when the two polymers are mixed together at certain ratios the release is in between [18, 19]. Therefore, the meaning of “control” remains imprecise since the diffusivity of the polymer dictate the release profile unless the diffusivity is changed by
physical or chemical modification within the polymer matrix. Modifying the processing variables and applying new techniques methods, accomplished by smart blender and polymer blend led to changes in diffusivity hence different release profiles were achieved [4].

Dr. Yam and Dr. Schaich group has developed a conceptual framework [Figure 1] as a guide and roadmap for advancing CRP technology concept and application. The usefulness of this framework stands out by illustrating the elements and variables involve in producing and of the major elements in CRP technology applications is the polymer. So far almost all polymers being used in CRP, specifically in food applications, are synthetics. Although synthetics polymers play a huge role in the area of food packaging, also represent a huge environmental concern [20]. This environmental concern is kept increasing for the last couple decades and consumer still looking for solutions desperately.

In recent years, development in the area of eco-friendly polymeric materials with exceptional properties has generally become subject of great interest in material and packaging sciences. Renewable polymers are the most promising candidates in these worldwide efforts. Such polymers are obtained from renewable sources that lead to sustainable development with smart technology in terms of economic and ecology. The motivation behind the interest in renewable polymer materials in both academia and industry are: biodegradability; advances research development in biodegradable materials; reduction in packaging waste volume; compostability in natural cycle; climate protection through reduction of released carbon dioxide; and possibility of application of agricultural resources for production of green packaging materials.
Some studies have been done exploring biodegradable polymers such as pectin, gelatin, chitosan, polylactic acid, and others [21-23]. Among those biopolymers, polylactic acid (PLA) shows potential to be used as food packaging material using the existing packaging machineries to extrude it [24].

PLA is a biodegradable polymer generally used in the field of drugs delivery, human tissue replacement, and medical devices for controlled release application, but recently, PLA utilization in food and beverage industries has shown potential as alternative for packaging and films material.

PLA is produced by the fermentation of sugar from starch containing materials such as sugar cane, potato, and corn into lactic acid followed by polymerization process to produce PLA. PLA believe to be among the most promising biodegradable polymers that someday might be an alternative for synthetic non-biodegradable polymers [25, 26], which help reduce the environmental concerns regarding landfill with food packaging plastics materials. Adding to its environmentally friendly nature, PLA can also be used for food contact surfaces and is generally recognized as safe (GRAS) by FDA [27, 28]. It does also provide packaging industry with a renewable sustainable option for a variety of uses. Many of these uses include flexible films. The combination of desirable properties such as high clarity, stiffness and excellent printability combined with the ability to process on conventional in many cases existing assets provide an opportunity for market leaders to bring innovative and environmentally friendly packaging options to market.
Figure 1: Conceptual framework/roadmap for CRP
The uniqueness of PLA that makes it a good candidate for CRP applications is embedded in its stereochemical compositions, L-lactic acid (P-LLA) and D-lactic acid (P-DLA), which certainly can be tailor made to alter its final properties [29]. Final properties, such as glass transition temperature \(T_g\), melting temperature \(T_m\), crystallinity% can significantly be affected by varying L and D ratios. PLA can be either amorphous or semicrystalline based on the amount of L, D, or/and meso-lactide in the structure, which mean that PLA can be easily produce completely amorphous or semicrystalline. PLA polymer with high crystallinity % are expected to deliver very slow or zero release due to the very packed and well-arranged crystal structure of the molecules, whereas polymer with amorphous structure or low crystallinity % delivers fast release most likely due to the chain mobility in the amorphous structure. To achieve different crystallinity %, the stereochemical compositions, which has notable influence on melting temperature \(T_m\), rate of crystallization, and ultimate extent of crystallization, can be varied and modified [30, 31] for the benefit of CRP. In addition, the final properties of PLA can be altered and modified by varying the processing conditions, which assist in determining the crystallization rates, crystalline structure, and morphology [32, 33] which are ultimately explain the uniqueness of PLA as a single polymer suitable for CRP applications to different food.

Though CRP as a technology has proven to be effective and work well, empirically and experimentally [18, 19, 34, 35], the answer to find a single polymer that can provide a wide range of release profile for different food applications is yet to be found. This dissertation consists of two major parts to address this issue. Part I discusses the attainment of a wide range of release profile of tocopherol from PLA films using solvent
casting method to produce the films and Part II discusses the comparison between solvent casting data vs. extrusion casting data in terms of release profile of tocopherol and the films properties.
2 LITERATURE REVIEW

Part I

2.1 Shelf Life of Food

Shelf life prediction of food from all sources (plant or animal) and kinds (fresh, semi-processed and processed) determines by three factors: food, package, and the environment [2]. Depending on the food type, the environmental factor plays a major role in shelf life determination [36] regardless of the packaging system, since the environmental factor involves elements such as temperature, oxygen, and relative humidity. The package role is only to protect the food against package-dependent deterioration modes and not the noncontrolled environments. After the product leaves the factory, temperature will start fluctuating: during transportation, unloading at retailer, from retailer to home (especially during summer), at home (fridge frequent opening and closing). So to envisage a shelf life of a food one should consider the noncontrolled environments, which is the degrading process for that particular food. Considering these factors, more innovative packaging systems are needed to address this issue and make the package respond to food and environment.

2.2 Innovations in Food Packaging

The innovations in food packaging and technology are based on the concept of making the package senses the environmental changes, both internally and externally, and respond to these changes by changing its own properties accordingly its internal
environment also changes [2, 37]. These innovations are not only driven by the four functions of the package but also driven by the prediction of shelf life for different type of food such as fresh, semi-processed, and processed foods and whether for civilian (during crises or normal life) or military (different war zones). Scientists in the areas of polymer science and packaging science & technology have developed different types of food packaging such as modified atmosphere packaging (MAP), vacuumed packaging (VP), controlled release packaging (CRP) which include antimicrobial and antioxidant packaging, …etc. to address the issues related to food quality retention and shelf life extension from farmer through retailer to consumer [3]. Among the new packaging technology systems, CRP is the newest packaging technology that emphasis beyond the four basic functions of food packaging.

2.3 Controlled Release Packaging (CRP)

Controlled release packaging (CRP) represents a new generation of functional packaging materials in which the package acts as a delivery system for active compounds such as antimicrobials and antioxidants. The active compound is released in a timely manner to enhance safety, retain quality, and extend shelf life of food. The application of controlled release has been effectively used in pharmaceuticals and drug industries for quite sometimes [5-17] while its application in food industry is relatively new.

Designing a CRP for food application is interesting but at the same time is very challenging, especially when the release profile of active compounds incorporated depends on the polymer type, structures, and morphology. These parameters determine the release rate or profile, besides the size of active compounds and storage temperature [19]. The ultimate concept of CRP is to manipulate polymer morphology to achieve the
required release kinetics (fast or slow release) to match the food type. In case of release profile of active compounds from synthetic polymers e.g. polypropylene (PP), high density polyethylene (HDPE), and linear low density polyethylene (LLDPE) individually Figure 2, the release is set to one profile either slow or fast, and when two polymers are blended together at certain ratios a third release profile will be obtained, Figures 3 [19].

![Graph](image)

**Figure 2:** Tocopherol release from different films into 95% ethanol at 40°C

Therefore, the meaning of “control” remains imprecise since the diffusivity of the polymer dictate the release profile unless the diffusivity is changed by changing polymer matrix either by physical or chemical modification. Modifying the processing variables and applying new techniques methods accomplished by smart blender and polymer blend led to changes in diffusivity hence different release profiles were achieved [4].
2.3.1 Previous Works on CRP

Our laboratory has done extensive researches on the concept of CRP applications in both antioxidants and antimicrobial in food simulants and real foods. The conceptual framework [Figure 1] was used as a roadmap for all researches that being conducted. The results are indeed support the concept and showed that CRP is actually effective.

2.3.1.1 Antioxidant CRP

Antioxidant packaging is type of CRP in which the antioxidant agents incorporated into the packaging matrix or coated onto the surface of the packaging material for sake of preventing or retarding the oxidation reaction. Another role of antioxidants when incorporated into the polymer matrix is to protect the package itself from oxidation.
To prove the concept of control or slow release effects versus instant addition Figure 4, Zhu et al (2008) reported that added 300 ppm of tocopherol at a rate of 50 ppm for 6 days every 24-hour has extended the induction period longer than the addition of 300 ppm tocopherol all at once [18].

The effectiveness of slow release from LDPE and PP films incorporated tocopherol versus instant addition of tocopherol in food simulant, linoleic acid, has been demonstrated by Zhang et al. (2004) and the result shows that slow release from films was more effective than instant addition in delaying oxidation Figure 4 [35].

2.3.1.2 Antimicrobials CRP

Antimicrobial packaging stand for a system that has ability to kill or inhibit the growth of microorganisms hence enhance the safety and quality of food and extend its shelf life.
Various antimicrobial compounds could be incorporated into polymer matrix to create antimicrobial packaging system, which hereby refer as CRP system.

Real Food System Experiment

1. Effect of EVA containing thymol on Salmonella

An experiment to evaluate the effect of EVA containing thymol on *Salmonella* inoculated tomato surface was conducted previously in our laboratory. The films (EVA containing 5 % thymol) were produced in Berry Plastics™ and the procedure used for microbial experiment is as described below:

Overnight culture was prepared and 5 ml was inoculated into 500 ml of 0.1% peptone buffer in a bag. Then tomato was added to the inoculated peptone buffer and hand pressed for 5 minutes and dried under laminar airflow hood for 24 hours. After that tomatoes were covered with EVA films with 5% thymol and without (control) and incubated for 24 hours. 25g of each tomato was weight and placed into 225 ml peptone buffer and stomached for 2 minutes, then plated on XLTA (media for isolation of non-typhi *Salmonella*) and incubated for 24 hours at 37 C and the colonies were counted. The result shows (unpublished data) an approximately two log reductions of *Salmonella* on the surface of tomato as a result of 5 % thymol containing EVA film Figure 5.
2. Effects of LDPE Containing Thymol and Carvacrol on Strawberry

Figure 6 below shows a result of Low Density Poly Ethylene (LDPE) polymer extruded with 3 % thymol and 3 % carvacrol as antimicrobial CRP packaging material to study their inhibitory effects on strawberry. Experiment was conducted at room temperature for 4 days. Thymol containing films was effective till day 3 and in day 4 the molds started to grow in carvacrol containing films too, while the control films was completely covered with molds.

The above two examples demonstrated the effectiveness of antimicrobial CRP in real food system. This success needs to be followed up and optimized since the release rate of the thymol and carvacrol from LDPE matrix need to be controlled specifically to match the mass transfer rate with the growth kinetics [38] of the molds or targeted microbe.
Model system experiment

Balasubramanian et al (2010) [39] studied the effectiveness of instant addition versus controlled release of nisin, an antimicrobial, on the growth of *Micrococcus luteus*, a microorganism used as a model in the study. A syringe pump was used to simulate release of nisin from the package system in a controlled release manner. According to
Figure [7], controlled release of nisin inhibited the growth of *Micrococcus luteus* gradually and maintained the inhibition constantly while instant addition shown a sharp inhibition and as soon as the nisin consumed the *Micrococcus luteus* started to grow gradually. This result presents more evidence to convince us that the concept of CRP is so far truthful and worthwhile. To apply CRP concept properly understanding factors affecting release kinetics is very necessary.

![Graph showing comparison between instant addition vs. slow release](image)

**Figure 7:** Comparison between instant addition vs. slow release

### 2.4 Major Factors Affecting Release Kinetics of Active Compound

#### 2.4.1 The Size of the Active Compound

The size of the active compound based on its molecular weight determines its
incorporation into the polymer matrix and its release. The release behavior is characterized by slow for large active compound and fast for small active compound.

2.4.2 Polymer/Active Compound Compatibility

By compatibility we refer to affinity of the active compound to react, chemically, with the polymer. Since in CRP the release of the active compound is the major driving force, physical entrapment is what is needed. Physical entrapment will allow the active compound to move freely within the polymer matrix while chemical interaction will not. In addition the active compound should not alter or change the polymer matrix in terms of appearance, mechanical properties, and barrier properties.

2.4.3 Polymer matrix

Polymer exists both in crystalline and amorphous forms. Since the entrapment of the active compound happens to be in the amorphous region of the polymer hence the amount of active compound incorporated is amorphous region dependence and not the crystalline region. Polymer crystallinity is one of the important properties of all polymers. Knowing the proportion of crystalline vs. amorphous regions of the polymer will play a great deal in determining the amount of active compound to be incorporated. The importance of this behavior can be explained by the example of polypropylene (PP), low density polyethylene (LDPE), and high density polyethylene (HDPE) incorporated tocoferol [19]. The release rate found to be followed the trend of LDPE > HDPE > PP. The explanation of this behavior is that based on the crystallinity % of each polymer which followed opposite trend of the release: PP > HDPE > LDPE.
2.4.4 Processing Method and Condition

Different methods of producing films are common practice in packaging plants such as extrusion (cast and blown) which determine by the end use of the packaging product. Based on the resins thermal properties e.g. melting and glass transition temperatures the condition of the extruder (barrel temperature and screw speed) will be adjusted [40]. These conditions will not be changed by large magnitude when mixing active compound with resin to be extruded. The intrinsic properties of active compound hinder the production of certain CRP materials without changing the method or condition. Some techniques use such as master batch to limit degradation and/or evaporation of volatile active compounds.

2.5 Packaging Materials

Packing materials properties are determined by their chemical structure, degree of polymerization, orientation of chain molecules, crystallinity, package density, and cross linking between individual molecules [2, 37, 41, 42] which bring plastics into the front choice when comes to different food packaging applications.

Synthetic or petroleum based plastics are extensively used for food packaging. However, due to their significant negative effects on the environment because of their slow degradation and the predicted end of the oil reserves in the whole world an alternative source for polymer is needed. The alternative source is found to be in the agricultural products from which bio-based or bioplastic that are renewable and at the same time degrade in a short time when exposed to a biologically active environment [21-23, 43].
2.6 Bio-based Polymer Materials

Bio-based polymers are made from annually renewable resources, such as corn, potato, and sugar cane, which are on the whole biodegradable or compostable on industrial composting sites [22, 44, 45]. During the last three decades bio-based polymers have seen a growing field of potential applications such as in medical, pharmaceutical, and food packaging. Few bio-based polymers fulfill with standard product specifications, which can be converted to packaging end products using the existing standard machinery for thermoplastics and just like conventional polymers, the bio-based polymers can easily be used for an enormous variety of products which paved the road for sustainability [46-51].

Sustainability is defined as “a development that meets the needs of the present world without compromising the needs of future generations”[2] and agricultural products fit into this definition completely such as corn that use to produce Polylactic acid (PLA). Most people when thinking about sustainable packaging they recall only the three elements of sustainability, which are environment, economy, and society and forgot to link them with the present and future use of food packaging. Bio-based polymers are still more expensive compared with oil based plastics, and to bridge that gap we need to add functionality to bio-based polymer.

As a result, a number of different types of bio-based polymers are now available on the market but so far PLA represent the front-runner among all bio-based plastics, especially for food packaging applications [27, 46, 52, 53].

PLA considered to be one of the leading drivers of the advances of bio-based polymers on the market [54]. It characterizes a new polymer generation and at present represents
the only commercially available biopolymer that made entirely from agricultural sources. It is also one of the most versatile materials [55-57] and in contrast to other available biobased it is also suitable for food packaging applications [49, 58-60].

2.7 Polylactic Acid Polymer

2.7.1 Lactic Acid

Lactic acid (2-hydroxypropanoic acid CH₃CHOHCOOH) is one of the smallest chiral molecules, which can be either of L (+) or D (-) stereoisomer, Figure 8. Lactic acid is produced naturally by animals, plants, and microorganisms [61]. It can also be originated from intermediates product (e.g. acetaldehyde, ethanol) or from coal byproducts (e.g. acetylene) or oil byproducts (e.g. ethylene) [62-64].

Lactic acid is distinguished by its three–carbon organic acid [61, 65]. The first “terminal-carbon is part of an acid or hydroxyl group, the third (considered the central-carbon) is part of an alcohol group while the second terminal-carbon represents a part of a methyl or hydrocarbon group” [66, 67]. Pure anhydrous lactic acid is non-volatile material that is
odorless and white (in color) crystalline salt. Lactic acid can be manufactured commercially by either chemical synthesis or fermentation of starch. The chemical synthesis produces two isomers or a racemic mixture, while the fermentation process results in an optically pure form of lactic acid or racemate. The fermentation process depends on nature of microorganisms, substrates and fermentation conditions used in the production process [68, 69]. The sources of the fermentative production of PLA are agricultural products such as 4sugars and starch, which are sustainable substrates. Chemical synthesis is considered not sustainable because they produced from petrochemical origin which are not a renewable sources [70].

The two functional groups of the lactic acid allow it to react and interact in different chemical reactions. The first reactions include condensation, esterification, reduction and substitution at the central-carbon which is the alcohol group [71]. These reactions allow lactic acid to be used for products with bulky quantity that can be used packaging materials. The microorganisms with their rapid and high growth rate are the best way of producing lactic acid in large scale to be used in packaging materials.

2.7.2 Polylactic Acid

Polylactic acid or polylactide (PLA) is linear aliphatic thermoplastic polyester as Figure 9 shows its chemical structures [72]. It is a bio-based polymer generally used in the field of drugs delivery, human tissue replacement, and medical devices for controlled release applications. Recently, PLA utilization in food and beverage industries has shown potential as packaging and films material [45, 65, 72].
PLA is produced by the fermentation of sugar into lactic acid followed by polymerization process to produce PLA. Polylactide-co-glycolide) is the biodegradable copolymer of PLA and polyglycolide (PGA). Biodegradable polymers have been suggested as controlled release systems for active compounds from the inner liner or coating of food packaging [21, 73]. Degradation of PLA and PGA begins by diffusion of water into the polymer, followed by random hydrolysis, material fragmentation, and finally a more extensive hydrolysis. The polymer degradation by-products, such as lactic acid, are common food ingredients, and the only expected effects would be an increase in the acidity of the food or beverage [74-76].

2.7.3 Synthesis of PLA

The two functional groups and the nature of chiral carbon of the lactic acid permit a wide range of chemical reactions for lactic acid. The primary classes of these reactions are condensation, esterification, reduction and substitution at the alcohol group [69, 75, 77, 78]. Using such reactions, lactic acid can be produced in large volume to be used as packaging materials.
PLA is synthesis by using anaerobic fermentation of sugars that derived from agricultural raw materials (renewable yearly) such as corn, sugar beet, sugarcane, potato, wheat, rice. The bacteria that responsible for this process are from genus *Lactobacillus* [1, 25].

The process of synthesizing PLA from P-LLA and/or P-DLA through direct condensation polymerization or polymerization through lactide formation, Figure 10, allows the producer to achieve different molecular weight (high or low) of PLA, which means that the production of P-LLA or P-DLA alone or a mixture is controllable and achievable [29].

![Diagram of PLA synthesis](image)

**Figure 10:** Synthesis of PLA from P-LLA and P-DLA. adapted from Lim *et al* [1]

### 2.7.4 Processing of PLA

PLA is satisfies the packaging industry’s requirements [79] by being processed by almost all processing methods, such as: injection molding, sheet/film extrusion, spinning, blown
molding, and thermoforming [80]. This property of processability makes PLA the front-runner compared with all others bio-based polymer [52, 65, 81]. Actually products made from PLA are already in the market including a variety of food packaging design.

### 2.7.5 Properties and Advantages

PLA, besides being thermoplastic, biodegradable, compostable its mechanical and barrier properties can be compared to synthetic polymers, Table 1, such as polystyrene (PS) and polyethylene terephthalate (PET) [80, 82]. Some economic studies show that PLA is feasible material economically for use as food packaging material. According to medical studies the migrations level of lactic acid to food from packaging polymers is very low compare with the amount being used in common food ingredients [27]. Consequently, polymers derived from lactic acid will cause no harm and can be used for packaging applications [83]. Currently, food-packaging polymer from PLA is being used for short-shelf-life products with common applications, such as containers, drinking cups, sundae and salad cups, overwrap and lamination films, and blister packages.

<table>
<thead>
<tr>
<th>Properties</th>
<th>PLA 4031-D</th>
<th>PLA 4041-D</th>
<th>PET</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_g$ (°C)</td>
<td>71.4</td>
<td>66.1</td>
<td>80</td>
</tr>
<tr>
<td>Relaxation enthalpy (J/g)</td>
<td>1.4</td>
<td>2.9</td>
<td>N/A</td>
</tr>
<tr>
<td>$T_m$ (°C)</td>
<td>163.4</td>
<td>140.8</td>
<td>245</td>
</tr>
<tr>
<td>Enthalpy of fusion (J/g)</td>
<td>37.5</td>
<td>21.9</td>
<td>47.7</td>
</tr>
<tr>
<td>Crystallinity percentage</td>
<td>40</td>
<td>25</td>
<td>38</td>
</tr>
</tbody>
</table>
2.7.6 Uniqueness of PLA

The uniqueness of PLA that makes it a good candidate for CRP applications is embedded in its stereochemical compositions, L-lactic acid (P-LLA) and D-lactic acid (P-DLA), which certainly can be tailor made to alter its final properties [29, 33, 84]. Final properties, such as glass transition temperature ($T_g$), melting temperature ($T_m$) Table 2, and crystallinity can significantly be affected by varying L and D ratios [60, 85]. PLA can be either amorphous or semicrystalline based on the amount of L, D, or/and meso-lactide in the structure, which mean that PLA can be easily produce completely amorphous or semicrystalline. Since amount of active compound incorporated into polymer is amorphous region dependence, PLA polymer with high crystallinity % are expected to be loaded with low amount of active compounds and being delivered in a very slow or zero release due to the very packed and well-arranged crystal structure of the molecules, whereas polymer with amorphous structure or low crystallinity % are expected to be loaded with high amount of active compound and being delivered in a fast release mode due to the chain mobility in the amorphous structure.

Table 2: Primary transition temperature of selected PLA copolymers

<table>
<thead>
<tr>
<th>Copolymer ratio (L/D,L)-PLA</th>
<th>$T_g$ (°C)</th>
<th>$T_m$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0 (L/D,L)-PLA</td>
<td>63</td>
<td>178</td>
</tr>
<tr>
<td>95/05 (L/D,L)-PLA</td>
<td>59</td>
<td>164</td>
</tr>
<tr>
<td>90/10 (L/D,L)-PLA</td>
<td>56</td>
<td>150</td>
</tr>
<tr>
<td>85/15 (L/D,L)-PLA</td>
<td>56</td>
<td>140</td>
</tr>
<tr>
<td>80/20 (L/D,L)-PLA</td>
<td>56</td>
<td>125</td>
</tr>
</tbody>
</table>
To achieve different crystallinity, the stereochemical compositions, which has notable influence on melting temperature ($T_m$) and rate of crystallization can be varied and modified [30, 31] for the benefit of CRP. In addition, the final properties of PLA can be altered and modified by varying the processing conditions, which assist in determining the crystallization rates, crystalline structure, and morphology [32, 33] which are ultimately explain the uniqueness of PLA that suit CRP technology for different food applications.

### 2.7.7 PLA Drawback

Although PLA has many advantages with respect to its biodegradability, processability with existing extrusions, and physical characteristics that makes it suitable for most food packaging applications; it still has a major critical drawback, which is its high brittleness that affects its applications for flexible food packaging such as thin film for wrapping food items [3, 24, 54, 86]. To overcome this impediment, several constituents have been studied and introduced as plasticizers. The plasticizers effect was characterized by a decrease on $T_g$ and an increase in chains mobility that lead to produce a flexible films. Some plasticizers have shown compatibility with PLA when applied at different levels of concentrations. They also have fewer effects on tensile properties, which are very important characteristic for flexible packaging applications [87, 88]. Many plasticizers have attempted to be used for PLA but without success. Polyadipates, a plasticizer, has shown its good compatibility with PLA [89].
Part II

2.8 Solvent vs. Extrusion Casting

2.8.1 Solvent casting

Solvent or solution casting is a very convenient method for thin film production. It is the oldest process in plastic films manufacturing that still widely used by many researchers [59, 90-97]. During the process of solvent casting the suspension of a polymer into a solvent involves two transport processes. First, the solvent diffuse into the entangled and coiled molecules and work its way to chain disentanglement in which the solvent break only the Van der Waals force between the molecules. When the polymer is in contact with solvent, the solvent will diffuse into the polymer and due to plasticization of the polymer by the solvent a gel-like swollen layer is formed along with two separate interfaces, one between the glassy polymer and gel layer and the other between the gel layer and the solvent. Mechanical stirring and time help polymer to dissolves more quickly [90].

The solution or polymer film is exposed to relatively low thermal or mechanical stress throughout the entire process. As a result, degradation (breaking of covalent bond) or adverse side reactions are insignificant.

Some important elements and requirements of solvent casting are:

1. Solubility of the polymer in a volatile solvent or water is obligatory

2. The solution should be stable with minimum viscosity is needed
3. Homogeneous film formation and release from the casting plate is required

To obtain such properties many process tricks can be used such as co-solvent systems, dissolution at overpressure, and use of specific molecular weight distributions of polymer or co-polymer, additive such as plasticizers, release agents [90].

The drying process in thermoplastic polymer-solvent systems displays different diffusion regimes. When solvent concentrations are high, the glass transition temperature falls below the process temperature. As a result the diffusion coefficient of the solvent in the film is high and rapid evaporation take place. Below a certain concentration limit and depending on the chemical nature of the combination e.g. near 3-6% residual solvent, the glass transition temperature rises to a temperature higher than process temperature. Even after a drying process with residual solvent of less than 5%, the film still has different properties at its airside and support-side surfaces, according to the film formation process.

The solvent diffusion coefficient of a given polymer-solvent combination is the crucial parameter governing production speed [87, 90, 93, 94].

**Major advantages and disadvantages of solvent cast films:**

- Consistent thickness
- High optical purity film
- Exceptional transparency
- Feasibility of producing thin films that difficult to produce by extrusion without stretching
- Not a suitable method to produce thick films.
Solvent casting is considered not cost effective method because it is slow production speed and the process of solvent recovery is an additional process, which adds to the cost of the production [90, 95, 98].

### 2.8.2 Extrusion Casting

Extrusion casting is a complete different process from solvent casting. Figure 61 shows a typical plastic extruder. Extrusion is the process where a solid resin, usually in the form of pellets, is fed through the hopper to a heated chamber contained a feed screw [1, 99, 100]. The resins melted due to two heating sources. The first source is the shear from the screw and the second source is the heated barrel. The speed of the feed screw and torque control is critical for quality of the final plastic material. As the resin is conveyed, it compressed, sheared and eventually melts, and then the melted resin is forced out of the chamber at a steady rate through a die. The chill rolls will immediate cool the melt and that will results in resolidification of plastic sheet or film [100].
Advantages and disadvantages of extrusion casting

Extrusion process provides opportunities to form different shapes of the end product with different properties. Orientation, quenching, and stretching are among the good way of changing the structure of the final sheet or film using extruder.

During extrusion of the polymer, the high shear rate induced orientation and chain alignment in addition to the rolls, which induced crystallization. The process is very complex and expensive and that’s why it’s very convenient to use solvent casting [100].
3 Hypothesis and Objectives

3.1 Hypothesis

According to above cited science based literature reviews and preliminary data obtained a hypothesis was formulated as follow:

• There is a gap in CRP technology that no single polymer can provide a wide range of release profile/rate suitable for different CRP applications. PLA with its unique chemistry could be that polymer, hence understanding its structural forming behavior will help in understanding the release kinetics of active compounds in a systematic manner.

• Since the stereochemical composition of PLA (L:D) is critical for controlling its structure [84] then by varying the ratio the structure will be changed which allow us to design a specific structure that provide a desired release profile for specific application.

• Existing PLA grades are varying in their thermal properties and this can be used for the advantage of CRP technology with extruder and incorporate different active compounds (volatile and nonvolatile) for different application.

3.2 Objectives

The long-term goal is to apply CRP concept using PLA, a single bio-based polymer, as a delivery system using different active compounds to acquire a wide range of release profile appropriate for various CRP applications.
3.2.1 The specific objectives

1) develop PLA containing tocopherol films by solvent and extrusion casting methods and investigate the effects of stereochemical composition (L and D) and processing conditions on thermal and physical properties of PLA films using solvent casting,

2) investigate the effects of stereochemical ratio (L and D) and processing conditions on thermal and physical properties of PLA films using solvent casting evaluate release and diffusivity kinetics of these films, and

3) Investigate the effects of processing methods (solvent and extrusion casting) on tocopherol release profile, film surface morphology, and thermo-mechanical properties.

First objective is to study the functional relationship between PLA stereochemical composition/ratio (P-LLA and P-DLA), which has significant effects on crystallization and melting temperature ($T_m$) and processing conditions (drying rates and annealing temperature) which determine: crystallization rates, crystalline structure, and final properties of PLA films morphology; and their effects on release profile of tocopherol in controlled release system. According to the literature, achieving this objective will guide us to attain different release profiles for tocopherol, which we are presuming to be a wide range as depicted in Figure 11.
The results are expected to help us in explaining the properties and performance of different commercial PLA grades and processing variables vis-à-vis release kinetics and diffusion coefficient of the films. It is important to reveal the effect of PLA stereochemical composition and its corresponding release profile in order to develop new forms of CRP using PLA as a delivery polymer.

The second objective is to evaluate the results of solution casting and extrusion casting methods of PLA containing tocopherol CRP films in terms of release profiles and thermo-physical properties.

Specifically, will investigate the effects of the two processing methods on PLA-CRP films, which include: release kinetics of tocopherol, thermal analysis of the films, film morphology, and mechanical properties.
The result of the second objective will help us in determining the viability of data obtained through solvent casting method.

### 3.2.1.1 Specific Tasks

- Produce CRP films from 100 % P-LLA, 100 % P-DLA and different combination ratios of P-LLA and P-DLA (100/0, 75/25, 50/50/, 25/75, and 0/100) using solvent casting method.
- Produce CRP films from commercial available PLA grades containing: 98 % P-LLA/2 % P-DLA and 92 % P-LLA/8 % P-DLA) using solvent and extrusion casting methods.
- Quantify total amount of tocopherol incorporated into the films (total extraction).
- Evaluate release kinetics and estimate the diffusivity of tocopherol in the films.
- Evaluate the effects of different combination ratios of P-LLA and P-DLA on release profile, diffusivity, mechanical and thermo-physical properties of the films.
- Evaluate the effect of processing conditions (drying rate and annealing) on the release profile, diffusivity, and thermo-physical properties (crystallinity, water vapor and oxygen transmission rates) of the films.
- Evaluate and compare the effects of processing method (solvent vs. extrusion) on the release profile, diffusivity, mechanical and thermo-physical properties of the films.
4 EXPERIMENTAL DESIGN

Part I & II

4.1 Materials and Methods

4.1.1 Materials

PLA resins contained 100 % P-LLA and 100 % P-DLA (named PLA) were purchased from Sigma-Aldrich, Allentown, PA; PLA resins contained 92 % P-LLA / 8 % P-DLA (named PLA1) and 98 % P-LLA / 2 % P-DLA (named PLA2) were purchased from NatureWorks™, Blair, Nebraska, USA; tocopherol was purchased from Cargill, Eddyville, Iowa, USA. Chloroform, ethanol, and methanol (all HPLC grades) were purchased from Fisher Scientific, Fair Lawn, New Jersey, USA.

4.1.2 Methods

4.1.2.1 Films Production

4.1.2.1.1 Resins drying

PLA is a hygroscopic material, which means that it absorb moisture from the atmosphere. The resin has to be dried overnight to get moisture level ~0.25%. 80lbs of the resins were dried in a small scale drier Figure 12, at ~49°C overnight and the level of the moisture reached 0.08%.
4.1.2.1.2 Solution casting

CRP films were prepared using a solution casting method. Five g of PLA resins were dissolved in 100 mL of chloroform while mixing with a magnetic stirrer in a volumetric flask at ambient temperature for 30-45 minutes. Then tocopherol (3000 ppm) was added to the solution and stirred for few more minutes to assure complete mixing of tocopherol within PLA solution. The dissolved solution was poured onto glass plates (16.5 cm X 16.5 cm X 0.4 cm) and Teflon Petri dishes and allowed to dry for 24 hours at ambient temperature. The dried films were peeled from the casting surfaces. To eliminate all solvent and moisture, the films then further dried in a vacuum chamber (LabLine Environers, 2219) at 40 °C for about 3-4 hours.

To visualize the process of solvent casting this schematic draw Figure 13 shows a polymer resin where the molecules are entangled and immersed into the solvent, the

Figure 13: Dryer used to dry resin before processing
solvent diffuse and disentangle the molecular chain where the outer layer of the resin became rubbery while the inner layer is glassy and by time and stirring the will finally reach a complete dissolution of the resin in the solvent.

During solvent casting, the solvent basically work into separation of the molecules clusters into individual molecules, which breaks the weak Vander wall forces and not the covalent bond. After drying, by evaporation, the PLA molecules form the clusters which form the film.

The films thicknesses were measured with a hand thickness measurement instruments (Fowler & NSK- Digitrix) in several locations and had an average of 109.22 µm.

The set of films was stored in a zipper plastic bag for further analysis. Samples were analyzed using transmission TGA and DSC for physical and thermal properties and UV/vis was used for quantifying release profiles of tocopherol.
4.1.2.1.2.1 Films Drying and Annealing

The mix solution of PLA and tocopherol was divided into two samples; the first one dried at ambient condition while the second sample was completely covered to create a stagnant condition; as PLA known to have slow crystal formation pattern, the basic idea is to achieve more crystalline regions in the final film. The drying rate then calculated using Mettler Toledo Scale equipped with Labview program and found to be 8 and 10g/h. The films were annealed by exposing them to a temperature up to 120° C for 24hr and let them cool slowly for about an hour. The purpose of annealing was to increase crystallinity%; crystallization temperature ($T_c$) of PLA is around 112-120° C.

4.1.2.1.3 Extrusion casting method

Tocopherol containing films were produced from a multiple screws extruder (Dr. Collin GmbH Coextruded – cast film line: 7-layer) using only one screw extruder to produce films with one layer. Dried barefoot PLA resins were mixed with tocopherol prior the extrusion. Extruder conditions were set based on the PLA extrusion specification Table 3. The die temperature was set at 430F. With a screw speed of 70 rpm, films with a thickness of 75 µm were obtained. The control films for were also produced with the same conditions (no tocopherol was added). All films were produced at Pliant Corporation (Chippewa Falls, WI, USA).
### Table 3: Extruder condition

<table>
<thead>
<tr>
<th>Barrel temp (°F)</th>
<th>Die temp (°F)</th>
<th>Screw speed (rpm)</th>
<th>Residence time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>460</td>
<td>445</td>
<td>215</td>
<td>1-2</td>
</tr>
</tbody>
</table>

![Actual extruder used in this study](image)

**Figure 15:** Actual extruder used in this study

#### 4.1.2.2 Total Extraction

**Flask Release Studies**

The method used is based on Obinata *et al* (2006) flask release studies method [19]. 95 % ethanol was used as food simulant in accordance with FDA recommendation for fatty
food simulant as depicted in Table 4.

**Table 4:** Recommended food simulants by FDA [101]

<table>
<thead>
<tr>
<th>Food type</th>
<th>Recommended simulant</th>
<th>Target packaging materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous and acidic foods</td>
<td>10% ethanol</td>
<td></td>
</tr>
<tr>
<td>Low and high alcohol foods</td>
<td>10 or 50% ethanol</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Food oil (corn oil, HB 307, Miglyol oil)</td>
<td></td>
</tr>
<tr>
<td>Fatty foods</td>
<td>95% or absolute ethanol</td>
<td>Polyolefins (LLDPE, HDPE, PP etc.) Vinyl acetate copolymers</td>
</tr>
<tr>
<td></td>
<td>50% ethanol</td>
<td>Poly vinyl chloride, Polystyrene, Poly ethylene terephthalate</td>
</tr>
</tbody>
</table>

Total amount of tocopherol in the films was measured by weighing one g of CRP films containing tocopherol immersed in 40ml of methanol after being cut into ~ 2 cm² and kept at 40 °C in a shaker (Thermo Scientific, Max Q 2000) with 100rpm to loosen PLA matrix and allow the tocopherol diffuse out to the solution and then the concentration was measured by UV/Vis spectroscopy (Shimadzu, UV 1700 Pharma Spec).

The aim of this step was to quantify the real amount of tocopherol incorporated and trapped into the PLA films matrices and to find out if there was any kind of loss during the processing. The loss could be in terms of oxidation/degradation or chemically (covalent) bonding of tocopherol with PLA. The second aim of total extraction is to confirm the success of incorporation process and production of CRP film, in addition to help in the quantification of release profile of tocopherol. Methanol was used because it’s more aggressive than ethanol and that makes it easy to open up the polymer network and
allow tocopherol to diffuse faster.

Two standard curves were made to be used in the quantification of the amount of tocopherol released into methanol for total extraction and into 95% ethanol Figure 15 for release monitoring over time.

![Standard curve of tocopherol in 95% ethanol](image)

**Figure 16:** Standard curve of tocopherol in 95% ethanol

### 4.1.2.3 Release Monitoring of Tocopherol Overtime

To determine the release profile or quantify release rate of tocopherol from PLA films, the following method was used.

Approximately 1g of film (2 cm²) was weighed and suspended into 40 ml ethanol (95%) as food stimulant. Samples were incubated at 37 °C in a rotary shaker at 100 rpm. Each hour, the quantity of tocopherol released from PLA films in the solvent was measured by UV/Vis spectroscopy (Shimadzu, UV1700 Pharma Spec). The monitoring was ended when 100% of tocopherol was released or a constant value was reached.
4.1.2.4 Diffusion of Tocopherol from PLA Films

The diffusion of tocopherol from the PLA films to 95 % ethanol was determined based on the release profile obtained. 95 % ethanol was chosen as simulant to have a system that assured the diffusion of tocopherol. Four replicates were carried out in each experiment, and all the storage conditions were controlled with a variation of 0.5 C. 100 rpm shaking speed was applied. Samples of ethanol were taken hourly during.

The migration process is described by the kinetic of the diffusion of tocopherol in the film which is expressed by D. Two analytical solutions for the Fick’s second law equation for diffusion in one-dimension and limited volume of film in finite Equation 1 and infinite Equation 2 volume of solution [2, 102] were used for determination of diffusion coefficients (D)

\[
\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1-\alpha)}{1+\alpha+\alpha^2 q_n^2} \exp \left\{ -D q_n^2 t/l^2 \right\} \quad \text{......................... 1}
\]

where \( \frac{M_t}{M_\infty} \) is the concentration of tocopherol diffused at time t, divided by the concentration of tocopherol diffused at equilibrium; \( l \) is the thickness of the PLA film and the \( q_n \)s are the non-zero positive roots of \( \tan q_n = q_n \) and \( \alpha \) is obtained from equation 2.

\[
\alpha = \frac{V_s}{K_{ps} V_p} \quad \text{................................................................. 2}
\]

where \( V_s \) and \( V_p \) are the molar volume of the simulant and the polymer, and \( K_{ps} \) is the partition coefficient of tocopherol between PLA and the 95 % ethanol Equation 3, which...
at lower concentration can be assumed constant and calculated from the ratio of the concentration of tocopherol in PLA \((C_p, \infty)\) and the 95 % ethanol \((C_s, \infty)\) at equilibrium.

\[
K_{p,s} = \frac{C_{p,\infty}}{C_{s,\infty}} \quad \cdots \quad 3
\]

In the case that the amount of 95 % ethanol can be considered infinite (i.e., \(\alpha >> 1\) since \(V_s >> V_P\) and/or \(K_{p,s} < 1\), Equation 1 can be simplified as:

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

Then after simplifying Equations 1 and 4 and converted into more simple form as in Equation 5, diffusion coefficient of tocopherol from PLA films were estimated [102].

\[
\frac{M_{f,t}}{M_{P,0}} = 4 \left(\frac{D t}{\pi L}\right)^{0.5} \quad \cdots \quad 5
\]

Where \(M_{f,t}\) is the amount (\(\mu g\)) of tocopherol in the food simulant at time \(t\) (s), \(M_{P,0}\) is the initial amount of tocopherol in the PLA film, \(D\) is diffusion coefficient of tocopherol in PLA film (\(cm^2/s\)), and \(L\) is thickness of the film (cm).

**4.1.3 Films analysis**

**4.1.3.1 Scanning Electron Microscopy (SEM)**

The SEM is a major imaging device that allows us to visualize very close the morphology of the films. The films were analyzed using a Quanta 200 FEG scanning electron
microscope (FEI Co., Inc., Hillsboro, OR), operated at a high vacuum with secondary
electron imaging mode. For the reason of increasing the electrical conductivity, the film
samples were coated with a thin layer of gold prior the test.

**4.1.3.2 Thermal properties characterization**

DSC analysis was carried out using a TA Instruments Q-2000 DSC on single punched out
disks from the films under nitrogen purge. The heating rate was 10 °C/minute from 0 to
200 °C and the cooling rate was 5 °C/minute. The crystallinity content (X %) has been
calculated based on 100% crystallinity = 93 J/g. The melting temperature (Tm), glass
transition temperature (Tg), and the crystallinity (Xc) percentage of the PLA films were
determined using a differential scanning calorimeter (TA Instruments Q-2000 DSC) on
single punched out disks from the films under nitrogen purge. Transition temperatures
were attained in agreement with ASTM D3418-03.

Crystallinity percentages were determined in accordance with ASTM D3417-99 and
Equation 6 [29, 76].

\[
Xc(\text{wt.} \%) = 100 \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0(1-x)}
\]

where \(\Delta H_m\) is the enthalpy of fusion, \(\Delta H_c\) is the enthalpy of cold crystallization, \(\Delta H_m^0\) is
the heat of melting of purely crystalline PLA (93.7 J/g) and x is the amount of tocopherol
in the sample. Values for \(T_g\), \(T_m\) and \(Xc\) were determined from the first heating cycle
where heating rate was 10 °C/minute from 0 to 200 °C and the cooling rate was
TG analysis was carried out to measure moisture content and the stability of PLA. The decomposition temperature (TD) and the temperatures where the samples lost almost 95% of the weight (i.e. T95 %) was obtained in accordance with ASTM E1131-03 using a TA Instruments Q-5000 TGA on single punched out disks from the films under nitrogen purge.

The specimens were heated at the rate of 5 °C/min within a range of 30 up to 800 °C and above 90psi. All tests were done in triplicate and data were analyzed with Universal Analysis Software (Version 5.1A).

4.1.3.3 Mechanical properties characterization

Samples were tested for their mechanical properties, which included tensile strength, elongation at break, tensile modulus and fracture energy. Tensile strength is the stress in tension that is required to fracture the sample. Elongation is defined as the strain at fracture. Tensile modulus is a physical quantity representing the stiffness of a material. It is determined by measuring the slope of the line of a stress-strain diagram. Fracture energy is defined as the energy needed to fracture the polymer samples. This physical quantity is often mentioned as “toughness”. Rectangular shaped samples (1 × 10cm) were cut with the long dimension parallel to the extruding direction. These properties were measured with a grip separation of 5 cm and a 5 mm/min strain rate (crosshead speed). An upgraded Instron mechanical property tester, model 1122 (Instron, Norwood, MA), and Testworks 4 data acquisition software (MTS Systems Corp., Minneapolis, MN) were used throughout this work. Tests were performed in a conditioned room at approximately 73° F and 50% RH. Each test was
conducted on five samples to obtain an average value.
5 RESULTS AND DISCUSSION

Part I

5.1 CRP Films Physical Appearance:

The first reflection of the effects of L and D ratio, drying rate variation and annealing process is on the physical appearances of the films.

Figure 16 shows film (a) made from PLA1 (92%L/8%D) is very transparent while film (b) made from PLA2 (98%L/2%D) is opaque. The clear difference in the transparency of the films is because of the differences in the amount of L and D ratio in each film, which indicate the effect of the ratio on the crystallinity content of the final film. This variation can be considered as an advantage for suitability of PLA films for different food applications.

Figure 17: Effect of L and D ratio on physical appearance (a. PLA1 and b. PLA2)
Figure 17 shows films made from same resin, film (a) before annealing and film (b) after annealing. The reason for the appearance difference is increase in crystallinity of the film after annealing. Annealing is a process in which the molecules tend to rearrange and pack in a well-organized manner that leads to form more crystals, which affect the appearance of the films and make it more opaque. It is a fact that amorphous PLA and low crystalline PLA are clear materials with high gloss, while highly crystalline PLA is an opaque white material.

Figure 18: Effect of drying rate on the appearance of the film made from PLA1

Variation on the drying rate (evaporation of the solvent) also has impact on the appearance of the films which illustrates in Figure [17 a and b]. Although the films are made from same polymer the differences showed up after changing the drying rate by magnitude of 2g/hr which is considerably small.
Figure [18 a and b], shows the effect of drying rate variation in the physical appearance of the films that made from PLA2 though the difference is not as clear as films made from PLA1 still we can see slight difference.

Figure 19: Effect of drying rate on the appearance of the film made from PLA2

Solvent evaporation rate has effects on the appearance of the final film; the faster the evaporation rate the amorphous the film will be, because the molecules have not enough time for rearrangement to create crystalline region, in contrast the slower the evaporation of the solvent the more crystalline region the film will have. This characteristic of transparency could be explored more when using these types of films for different applications, especially with product that needed to be seen by consumer.
5.2 Film Thickness

The thicknesses of the films were measured at several different locations using a hand thickness measurement instrument and an average of 10 points was taken which had an average of 109.22 µm.

5.3 Total Extraction of Tocopherol:

Tocopherol amount incorporated into the films was measured using total extraction method in methanol. The result showed, Tables 5 and 6, that almost 100% of tocopherol has been recovered from all film samples produced by solvent casting, indicating that there was no lost during the process of producing and annealing of the CRP films. This result was expected based on PLA and tocopherol molecular structure where there is only physical entrapment and no chemical interactions or bonding of any kind that hindering the release of tocopherol. Beside the film has produced in dark environment which eliminate or reduce the chance of tocopherol to be oxidized by light and since tocopherol is very stable at high temperature we did not expect any kind of degradation at the level of temperature that the films produced and analyzed.

The result of extruded PLA showed that more than 90% of tocopherol has been recovered from all film samples produced by extrusion casting Table 7, indicating that there little amount of tocopherol that lost was during the preparation of mixing process of PLA resin with tocopherol. This result was also expected based on PLA melting temperature that requires low extrusion temperature at which tocopherol is quite stable.
Table 5: Tocopherol recovery from total extraction from PLA1 and PLA2 produced by solvent casting

<table>
<thead>
<tr>
<th>Drying rate (g/hr)</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA1</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>99.4</td>
</tr>
<tr>
<td>10*</td>
<td>99.7</td>
</tr>
<tr>
<td>8</td>
<td>99.3</td>
</tr>
<tr>
<td>8*</td>
<td>99.1</td>
</tr>
<tr>
<td>PLA2</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>99.7</td>
</tr>
<tr>
<td>10*</td>
<td>99.5</td>
</tr>
<tr>
<td>8</td>
<td>98.9</td>
</tr>
<tr>
<td>8*</td>
<td>99.2</td>
</tr>
</tbody>
</table>

*Annealed sample
Table 6: Tocopherol recovery from total extraction from PLA and its different L and D composition produced by solvent casting

<table>
<thead>
<tr>
<th>PLA and co-polymer ratio</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% L</td>
<td>98.8</td>
</tr>
<tr>
<td>100% L*</td>
<td>99.2</td>
</tr>
<tr>
<td>100% D</td>
<td>99.5</td>
</tr>
<tr>
<td>100% D*</td>
<td>97.9</td>
</tr>
<tr>
<td>50% L 50% D</td>
<td>99.7</td>
</tr>
<tr>
<td>50% L 50% D*</td>
<td>99.8</td>
</tr>
<tr>
<td>75% L 25% D</td>
<td>96.8</td>
</tr>
<tr>
<td>75% L 25% D*</td>
<td>97.8</td>
</tr>
<tr>
<td>25% L 75% D</td>
<td>98.2</td>
</tr>
<tr>
<td>25% L 75% D*</td>
<td>98.2</td>
</tr>
</tbody>
</table>

*Annealed sample

Table 7: Tocopherol recovery from total extraction from PLA and its different L and D composition produced by extrusion casting

<table>
<thead>
<tr>
<th>PLA film</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA1</td>
<td>94.6</td>
</tr>
<tr>
<td>PLA1*</td>
<td>93.2</td>
</tr>
</tbody>
</table>

*Annealed sample
5.4 Release Monitoring of Tocopherol Overtime:

5.4.1 Result of Solvent Casting Films

5.4.1.1 Effect of L and D Ratio on Tocopherol Release Profile from Pure PLA

The release profile of films made from 100 % P-LLA, 100 % P-DLA and different composition (100/0, 0/100 50/50, 75/25, and 25/75) was quantified. Experiments were performed in triplicate and the error bars represent standard deviation.

The result of the release profile of tocopherol is shown in Figure 19. Film made from 100 % L released 80 % of tocopherol in 60 hours and after annealing it released 35% only in the 60 hours. The film made from 100% D released around 70% and after annealing it released only 25% in 60 hours.

Overall, the result of release kinetics of tocopherol from films made from PLA with different ratios of L and D before and after annealing showed a varied range of release profiles. This wide range of release profile is the result of L and D ratio and annealing process, which allow the rearrangement of the molecular chains conformation. This conformation made the crystalline domains hinder the mobility of amorphous chains consequently affects the migration or diffusion of tocopherol through its matrices.

The formation of stereocomplex, which add more crystallinity to the film matrix is also responsible from this diverse release profile.
5.4.1.2 Effect of L and D Ratio on Tocopherol Release Profile from PLA1 and PLA2

The release profiles of tocopherol from PLA1 and PLA2 were quantified using flask method. Experiments were performed in triplicate and the error bars represent standard deviation.

Figure 20 shows the release profile of tocopherol from PLA1 and PLA2 dried at same drying rate (10g/hr) which indicate the difference between the two grades of PLA and how this difference reflect on the release kinetics of tocopherol. Although the two polymers share same trend till 9 hours and then PLA2 started release slowly compared with PLA1 and at hour 35 the difference in release amount is exactly 10%.

This behavior could be explained in combination with result of crystallinity % of each film. In fact, PLA1 has less crystallinity % compared with PLA2 and that explain why
PLA2 film release slower than PLA1 film. The 10 % seems not a huge difference but might have different effects in terms of shelf life extension.

5.4.1.3 Effect of Drying of Rate on Tocopherol Release Profile

The effect of drying rate on release profile of tocopherol is projected in Figure 21 signifying the impact of on factor of processing condition on release profile of tocopherol which in fact a reflection of the PLA structural changes. During the course of processing of the film the molecules are rearranging themselves based on the time allocated before complete evaporation of the solvent. From the graph different trends of release profile can be seen even between same PLA grades. PLA1 dried at rate of 8g/hr released 90% of tocopherol within 35hr, while same PLA1 dried at rate of 10g/hr released 100% of tocopherol at same period of time which is 35hr. PLA2 dried at the rate of 8g/hr released 80% of tocopherol in 35hr and when dried at rate of 10g/hr released everything within

![Figure 21: Effect of L and D ratio on tocopherol release](image)
The release profiles from PLA1, shows a release of 100% of tocopherol from films dried at rate of 10g/hr after 33hr, while the films dried at rate of 8g/hr showed a release of 90% for the same period of time, which means the drying rate did affected the structure of the films at molecular level and that translate into crystallinity % of each film. In another word, PLA is known to be a slow crystallize material [103] hence drying at rate of 10g/hr removed the solvent rapidly and that affects the crystallization process and provides amorphous structure then provide fast release compared with drying at rate of 8g/hr that provide semicrystalline structure consequently offer slow release.

![Figure 22: Effect of drying rate on release profile of tocopherol in PLA1 and PLA2 dried at different rates](image)

### 5.4.1.4 Effect of Drying and Annealing on Release Profile from PLA1 and PLA2

The effects of drying and annealing on release profile of tocopherol are shown in Figure 22. The range of release profile covers from 15 to 100% within 33hr. The drying rate
made a difference in the tocopherol amount released by 10% within 33hr, which can be seen in the first two plots (dried at 10g/hr, released 100% and at 8g/hr, released 90%), while annealing process made a difference of almost 80% for the same period of time (plots 1 released 100% and 3 released 35%; plots 2 released 90% and 4 released 13).

![Figure 23](image.png)

**Figure 23**: Effect of drying and annealing on release profile of tocopherol from PLA1

Figure 23 shows the combine effects of drying rate and annealing of PLA2 on the release profile of tocopherol. The same effects of drying rate have observed here too but with different trend profiles. The difference in the amount of tocopherol released is obvious in the first plot (dried at 8g/hr) that reaches 100% in 8 hours and in the second plot (dried at 10g/hr) that reaches only 80% in 33 hours. The annealing process also made a difference in the amount released that can be seen between first (released 100% in 8hr) and third (released only 15% in 33hr) plots and second (released 80% in 33hr) and forth (released only 5% in 33hr) plots.
The difference between Figures 22 and 23 can be taken as the reflection of the effects of L and D on release profile of tocopherol. The explanation of these differences in the release profiles could be linked to the increase in crystallinity due to the slow drying rate, annealing, and L and D ratio. Slow drying and annealing process increase the chances of molecules to rearrange and align to form more crystalline region that hinder the diffusion of tocopherol. The more the L content the more the crystalline region formed, which explain the difference in the release of tocopherol.

The data obtained from DSC experiment actually supported this theory of more crystalline lead to slow the release of tocopherol.

**Figure 24:** Effects of drying and annealing on release profile of tocopherol from PLA2
Figure 24 shows the combine effects of processing conditions (drying rate and annealing) and L and D ratio of PLA1 and PLA2 on the release profile of tocopherol. These results show a clear differences pattern of tocopherol release profiles, e.g. a range from 1 to 100% was achieved within 8 hours. Apparently the processing conditions (drying rate and annealing) show stronger effects than stereochemical composition (P-LLA and P-DLA). Since the range of the stereochemical composition used in this study is very narrow (92-98), more effects will be expected when the range is extended more (e.g. 80-99).

5.4.2 Result of Extrusion Casting Films

5.4.2.1 Effect of Annealing on Tocopherol Release

The result of the release of tocopherol from the extruded film was successful. This result shows the capability of the PLA film to release tocopherol from extruded films. The film
after annealing process showed a slower release profile. Annealing process induced crystallinity that led to affect the migration of tocopherol through the film. Figure 25 shows the result of tocopherol released from PLA before and after annealing process. 40% of tocopherol was released in 35 hours, while only 12% was released after annealing process for same period of time. Almost 30% difference was observed and this number can be changed, either decrease or increase by the annealing process to fit the required application.

![Figure 26: Release profile of tocopherol from PLA1 before and after annealing](image)

5.5 Diffusivity Estimation:

By using Crank’s model for diffusivity estimation, we were able to calculate the diffusivity of all samples using tocopherol release kinetics data. The model was simplified into Equation 5 and then used to calculate the diffusion coefficient as shown in
Figure 26, which illustrates the estimated diffusivity of tocopherol release profiles based of Fick’s second law of diffusion. The unannealed films appear to have some remaining solvent which might have acted as plasticizers leading to fast release of tocopherol, while the annealed films besides losing any solvent it built more crystalline content that lead to slow the release of tocopherol. The estimated diffusivity profiles is happened to be fitted the real data profiles very well which indicated that the release of tocopherol from the PLA films is generally due to the diffusion process.

The plots represent the fractional release of $\frac{M_t}{M_\infty}$ vs. $t^{0.5}$ were represented in dashed lines, indicating that tocopherol release was controlled by Fickian diffusion. The diffusion coefficient values of all films samples were found to be ranged between $2.42 \times 10^{-19}$ and $8.68 \times 10^{-16} \text{ m}^2/\text{s}$ as shown in Table 8.
Table 8: Diffusivities of tocopherol from different films

<table>
<thead>
<tr>
<th>Drying rate (g/hr)</th>
<th>Diffusivity (m^2/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA1</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>2.17x10^{-16}</td>
</tr>
<tr>
<td>10*</td>
<td>2.22x10^{-18}</td>
</tr>
<tr>
<td>8</td>
<td>7.01x10^{-16}</td>
</tr>
<tr>
<td>8*</td>
<td>1.40x10^{-17}</td>
</tr>
<tr>
<td>PLA2</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1.87x10^{-16}</td>
</tr>
<tr>
<td>10*</td>
<td>2.42x10^{-19}</td>
</tr>
<tr>
<td>8</td>
<td>8.68x10^{-16}</td>
</tr>
<tr>
<td>8*</td>
<td>2.35x10^{-18}</td>
</tr>
</tbody>
</table>

*Annealed sample

The unannealed films appear to have some remaining solvent which might have acted as plasticizers leading to fast release of tocopherol, while the annealed films besides losing any solvent it built more crystalline content that lead to slow the release of tocopherol. The estimated diffusivity profiles is happened to be fitted the experimental data profiles very well which indicated that the release of tocopherol from the PLA films is generally due to the diffusion process.

This diverse range of diffusivity values attributed to the differences in L and D content in PLA1 and PLA2 and crystallinity content in each film. In fact this result represents the effects of changes in L and D ratio, drying rates and annealing conditions on the diffusion coefficient of the films, which in return broaden the range of tocopherol release profile from 5 to 100% as presented above in Figure 26.

Generally speaking, tocopherol diffusion through crystalline structure is considerably
slower in comparison with diffusion through amorphous structure due to chain mobility.

5.6 Scanning Electron Microscopy (SEM)

5.6.1 Result of PLA1 and PLA2 Produced by Solvent Casting

To further understand and support the result of total extraction and release of tocopherol and assure the homogenous distribution of tocopherol into the film, the morphology of the films was observed by SEM as shown in Figures 27-30.

Figure 27 a and b shows the images of SEM obtained for PLA1 films samples. Both samples were dried at 8g/hr and sample b was annealed to achieve different properties in terms of crystallinity, melting and glass transition temperatures. The major purpose of these images was to understand the incorporation of tocopherol into PLA matrix and visualized the differences occurred on PLA morphology due to differences in L and D ratio and processing conditions.

![Image of SEM images](image)

**Figure 28:** a. PLA1-8g/hr and b. PLA1-8g/hr annealed
Figure 28 a and b illustrate the SEM images of PLA2 films samples. Both samples were dried at rate of 8g/hr and sample b was further annealed for the purpose of obtaining different morphology.

Figure 29: a. PLA1-10g/hr and b. PLA1-10g/hr annealed

Figure 30: a. PLA2-8g/hr and b. PLA2-8g/hr annealed

Figure 29 a and b illustrates the SEM images of PLA2 films samples dried at 8g/hr. The
samples b was further annealed for the purpose of obtaining different morphology. The same process occurred in sample dried at rate of 10g/hr, Figure 30.

Though from the images not much can be told, tocopherol is assumed to be well incorporated into the PLA matrix as shown on the homogeneous films surface morphologies. The differences observed between figures a (before annealing) and b (after annealing), are because of the annealing process, which induced more crystalline in the film matrix in addition to the variation in the ratio of L and D, which also resulted in differences in crystallinity content. No phase separation was occurred which indicate the homogeneous incorporation of tocopherol into films matrices. Although a qualitative correlation between annealing and release profile is found to be more realistic (annealing slow down the release of tocopherol), we have not yet been able to draw a direct quantitative correlations from the results of the SEM images.

![Figure 31: a. PLA2-10g/hr and b. PLA2-10g/hr annealed](image)
5.6.2 Result of PLA1 Produced by Extrusion Casting

The extruded PLA images show smooth homogeneous surface topographies. The rolls of the extrusion machine created these surfaces. Figure 31, a and b, illustrates the microstructure of the PLA film before annealing and Figure 32, a and b, after annealing with different magnification scale. It is clear that the density and size of spherulites increase with annealing. At higher magnification the crystals and spherulites are clearly visible. These results are supporting the data of release study where annealing decrease the amount released with time.

Figure 32: PLA1 before annealing
Although a qualitative correlation between annealing and release profile is found to be more realistic (annealing slow down the release of tocopherol), we have not yet been able to draw a direct quantitative correlations from the results of the SEM images.

It appeared that SEM alone could not help to localize tocopherol within the PLA matrix. Some other techniques or instruments might be appropriate to analyze the tocopherol localization and distribution within PLA matrix. Furthermore, some other supportive methods, such as FT-IR, Raman spectroscopy, or confocal microscopy might need to be used to co-analyze with SEM for better result and confirmation.

**Figure 33**: PLA1 after annealing
5.7 Thermogravimetric (TG)

The result of thermogravimetric analysis is shown in Figure 33 that represents the initial weight loss. The weight loss most probably represents the moisture since we did not expect any solvent (chloroform) residue as the samples were further dried at 40° C for 3-4 hours, which left us with moisture residues option. In addition PLA is known to absorb moisture from the atmosphere which supports our assumption.

![Figure 34: TGA result shows the initial weight (moisture) loss](image-url)

Samples were not homogenous enough to reliably report decomposition onset values as initially hoped but still can see the degradation started around 300° C. Residual moisture were found at a 5-10 % level in the films that were not annealed. Annealing lowered the level of residual moisture to 0.3 - 0.6 %, Table 9.
Table 9: The Result of TGA Shows the Initial Weight (moisture) Loss

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>% Initial Loss</th>
<th>T_{donset} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA1-10g/h</td>
<td>9.29</td>
<td>330.05</td>
</tr>
<tr>
<td>PLA1-10g/h*</td>
<td>0.54</td>
<td>328.70</td>
</tr>
<tr>
<td>PLA1-8g/h</td>
<td>9.00</td>
<td>330.11</td>
</tr>
<tr>
<td>PLA1-8g/h*</td>
<td>0.39</td>
<td>328.40</td>
</tr>
<tr>
<td>PLA2-10g/h</td>
<td>6.76</td>
<td>330.14</td>
</tr>
<tr>
<td>PLA2-10g/h*</td>
<td>0.26</td>
<td>326.70</td>
</tr>
<tr>
<td>PLA2-8g/h</td>
<td>5.82</td>
<td>326.97</td>
</tr>
<tr>
<td>PLA2-8g/h*</td>
<td>0.28</td>
<td>322.37</td>
</tr>
</tbody>
</table>

*Annealed sample

5.8 Differential Scanning Calorimetry (DSC)

5.8.1 DSC Result of PLA Produced by Solvent Casting

Films were analyzed by DSC to determine their thermal properties and quantifying the crystallinity content. This step is very crucial since the crystallinity indeed affect the release of tocopherol from PLA films. Table 9 shows the result of DSC experiment to reveal the thermal properties of the films made with different ratios of L and D. All thermograms Figures 34-43 were complex with typically multiple melting, cold crystallization and crystallization transitions occurring during the melting scans. Transitions from the 1st heating scan are reported in this table. All samples had a single glass transition temperature due to the different stereotactic configuration, while sample
made from 100% L or D had a single melting temperature, the films with mixture ratio had two melting temperatures Figures 38-43, first one represents homo crystal formation and the second indicate formation of stereocrystals.

To induce different crystallization by solvent or extrusion casting:

Fast solvent evaporation from cast film of L and D mixtures usually induces rapid homocrystallization together with stereocomplexation. To obtain exclusive stereocomplexation, the solvent needs to be evaporated slowly, or isothermally crystallized in a mixture of poor and good solvents.

Application of strong shear to the melt blend of L and D is effective in inducing predominant stereocomplexation because the macromolecular chains are extended (oriented) and that facilitates the interaction between the enantiomeric sequences and enables the subsequent stereocomplex formation.
Table 10: Thermal properties of pure PLA and its different ratios

<table>
<thead>
<tr>
<th>PLA Sample</th>
<th>$T_g$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$T_{msc}$ (°C)</th>
<th>$\Delta H_{msc}$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% L</td>
<td>45.5</td>
<td>173.9</td>
<td>34.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100% L*</td>
<td>58.8</td>
<td>176.2</td>
<td>37.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100% D</td>
<td>45.3</td>
<td>176.4</td>
<td>33.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100% D*</td>
<td>62.0</td>
<td>176.8</td>
<td>36.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50% L 50% D</td>
<td>44.7</td>
<td>175.3</td>
<td>23.1</td>
<td>215.7</td>
<td>14.8</td>
</tr>
<tr>
<td>50% L 50% D*</td>
<td>51.8</td>
<td>176.7</td>
<td>40.1</td>
<td>216.5</td>
<td>9.2</td>
</tr>
<tr>
<td>75% L 25% D</td>
<td>45.1</td>
<td>174.4</td>
<td>25.0</td>
<td>215.5</td>
<td>13.2</td>
</tr>
<tr>
<td>75% L 25% D*</td>
<td>76.2</td>
<td>176.5</td>
<td>37.9</td>
<td>216.3</td>
<td>12.0</td>
</tr>
<tr>
<td>25% L 75% D</td>
<td>46.4</td>
<td>176.3</td>
<td>26.6</td>
<td>217.4</td>
<td>10.8</td>
</tr>
<tr>
<td>25% L 75% D*</td>
<td>53.3</td>
<td>176.8</td>
<td>35.7</td>
<td>217.0</td>
<td>13.5</td>
</tr>
</tbody>
</table>

*Annealed sample
The thermograms in Figures 34-43 show the variation in thermal properties of 100% PLLA and 100% PDLA and their different composition.

Figure 35: DSC histogram of PLA 100/0 L/D
**Figure 36:** DSC histogram of 100/0 L/D annealed

**Figure 37:** DSC histogram of 0/100 L/D
Figure 38: DSC histogram of 0/100 L/D annealed

Figure 39: DSC histogram of 50/50 L/D
Figure 40: DSC histogram of 50/50 L/D annealed

Figure 41: DSC histogram of 75/25 L/D
Figure 42: DSC histogram of 75/25 L/D annealed

Figure 43: DSC histogram of 25/75 L/D
**5.8.1.1 Crystallinity Differences in Pure PLA**

In Figure 44, all films with different ratio or content of L and/or D represented with the black color while the annealed films represented with the gray color and as we can see the increase in crystallinity content in all films, which indicate clearly the changes in structure of PLA due to the effects of annealing on the films properties by letting the lactic acid molecules rearrange themselves and change their alignments in different packing positions leading to crystalline content increase.
5.8.2 DSC Result of PLA1 and PLA2 Produced by Solvent Casting

DSC analysis was used to determine thermal properties of the samples. All thermograms Figures 45 – 52, before and after annealing, were complex with typically multiple melting, cold crystallization, and crystallization transitions occurring during the melting scans. Transitions from the first and second heating scan are reported. All samples had a single glass transition temperature \( T_g \) during the cooling scan. Both unannealed samples for PLA1 have a lower \( T_g \) and lower degree of crystallinity than the annealed samples in the first heat. Similar behavior is shown in PLA2 samples, although the unannealed crystallinities are higher than for PLA1 Table 11.

The increase in crystallinity indicated by the annealing process looks about the same for PLA1 samples and PLA2 sample dried at 8g/hr. However, a significantly lower increase in crystallinity from annealing is seen for PLA2 at 10g/hr drying.

Figure 45: Effects of L and D ratio and annealing on crystallinity content
Overall, the increase in $T_g$ with annealing is qualitatively consistent with the fact that crystallinity is increasing. However, the increase in $T_g$ and increase in $\Delta H$ do not correlate well between the two materials and that because of the amount of P-LLA & P-DLA ratios in each PLA.

The second heat shows all eight materials to have the same $T_g$, however, all of the PLA1 samples are amorphous ($\Delta H \sim 0$), and all of the PLA2 samples (except for the last) show the same crystallinity as did before the first heating. This would seem to indicate that this materiel can crystallize much easier than PLA1.
Figure 46: DSC histogram of PLA1 dried at 10g/hr

Figure 47: DSC histogram of PLA1 dried at 10g/hr and annealed
Figure 48: DSC histogram of PLA1 dried at 8g/hr

Figure 49: DSC histogram of PLA1 dried at 8g/hr and annealed
Figure 50: DSC histogram of PLA2 dried at 10g/hr

Figure 51: DSC histogram of PLA2 dried at 10g/hr and annealed
Figure 52: DSC histogram of PLA2 dried at 8g/hr.

Figure 53: DSC histogram of PLA2 dried at 8g/hr and annealed.
Table 11: DSC results of first and second heating of PLA1 and PLA2

<table>
<thead>
<tr>
<th>PLA Sample</th>
<th>Drying Rate</th>
<th>Annealing</th>
<th>1st Heat</th>
<th>2nd Heat</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>T&lt;sub&gt;g1&lt;/sub&gt; (°C)</td>
<td>T&lt;sub&gt;m1&lt;/sub&gt; (°C)</td>
</tr>
<tr>
<td>PLA1</td>
<td>10g/hr</td>
<td>No</td>
<td>34.0</td>
<td>146.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Yes</td>
<td>61.7</td>
<td>146.1</td>
</tr>
<tr>
<td></td>
<td>8g/hr</td>
<td>No</td>
<td>34.6</td>
<td>148.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Yes</td>
<td>61.3</td>
<td>149.7</td>
</tr>
<tr>
<td>PLA2</td>
<td>10g/hr</td>
<td>No</td>
<td>46.0</td>
<td>167.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Yes</td>
<td>69.0</td>
<td>168.5</td>
</tr>
<tr>
<td></td>
<td>8g/hr</td>
<td>No</td>
<td>53.3</td>
<td>168.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Yes</td>
<td>64.8</td>
<td>166.8</td>
</tr>
</tbody>
</table>
5.8.2.1 Crystallinity Differences in PLA1 and PLA2

5.8.2.1.1 Effect of L and D on crystallinity content

The effect of variation in P-LLA & P-DLA ratio showed that PLA2 have double crystallinity% of PLA1 as shown in Figure 53, which emphasis the significant impact on of L and D ratio on the crystallinity%. PLA1 showed a 22% while PLA2 showed 41% crystallinity. This difference in crystallinity% is due to the fact that higher P-LLA content inherent higher crystallinity%.

5.8.2.1.2 Effect of Drying Rate on Crystallinity Content

The drying rate shows slight difference in PLA1 whereas no difference in PLA2 in terms of crystallinity % Figure 54 and that might be due to high L content in PLA2. The impact of drying rate on crystallinity content is not as clear as its effect on the release profile but might have effects on the crystals or/and spherulites shape and type.
5.8.2.1.3  Effect of Annealing on Crystallinity Content

Figure 55 shows crystallinity % changes provoked by annealing process from 22 to 31% are significant in PLA1 at both drying rates (8g/hr and 10 g/hr). This profile illustrates the effect of annealing, which adds more crystallinity% to the structure thereby affected the release profile of tocopherol. Actually this result is in consistent with result of release study.

The crystallinity % increase in PLA2 dried at 8g/hr from 40 to 54% surprisingly it did not change that much in sample that dried at 10g/hr Figure 55. Increasing crystallinity % followed the release profile pattern by widening the release range of tocopherol.
**Figure 56:** Effect of annealing on crystallinity\% of PLA1

**Figure 57:** Effect of annealing on crystallinity\% of PLA2
5.8.3 DSC Result of PLA Produced by Extrusion Casting

The DSC histogram regarding the films that produced using extrusion casting method is shown in Figures 57-60. The loading of tocopherol in the film showed no effect in terms of crystallinity content and the integrity of the film. No change in thermal properties of the films is observed based on the result of film with and without tocopherol.

The result indicates that annealing of extruded film is also increase crystallinity content, which is in consistent agreement the result of release study that showed annealing decreases or slows the release of tocopherol from the film matrix.
Figure 58: DSC histogram of extruded PLA with
Figure 59: DSC histogram of extruded PLA with tocopherol annealed
Figure 60: DSC histogram of extruded PLA without tocopherol
Figure 61: DSC histogram of extruded PLA without tocopherol annealed
5.9 Water Vapor and Oxygen Transmission Rates

The water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) were also found to be affected by annealing process as shown in Table 12.

Table 12: WVTR and OTR of PLA1 and PLA2

<table>
<thead>
<tr>
<th>Sample condition</th>
<th>WVTR (^2), g/100in (^2)/day</th>
<th>OTR (^2), cc/100in (^2)/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Before annealing</td>
<td>4.7</td>
<td>38.7</td>
</tr>
<tr>
<td>After annealing</td>
<td>2.5</td>
<td>8.0</td>
</tr>
<tr>
<td>PLA2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Before annealing</td>
<td>4.9</td>
<td>22.2</td>
</tr>
<tr>
<td>After annealing</td>
<td>2.9</td>
<td>9.0</td>
</tr>
</tbody>
</table>

The result of OTR shows more reduction compare with WVTR which is low from first place. These data are found to be comparable with literatures. As polymer morphology plays a fundamental role in barrier properties since annealing increase crystallinity and decrease permeability, the PLA final properties can be changed and modified by determination of L and D ratio and processing condition. The unannealed film can be used as CRP layer while the annealed one can be a barrier layer for multiple layers CRP-film.
5.10 Mechanical properties

Table 13 is the result of the mechanical test for the films produced with solvent and extrusion casting.

It is very important to run mechanical test for PLA films, regardless of the processing method, because PLA has to resist mechanical loads during filling, loading, and transportation and this require certain minimum mechanical properties.

Samples were tested for their mechanical properties to see how strong or tough the films based on the two methods. Both methods characterized by good mechanical properties, with tensile strength of 50-60MPa and elastic modulus of 3000MPa. However, the film shows low elongation at break which is typical of PLA and that one of the drawback of PLA which limits some of its uses. The explanation of why we see differences in the elongation between solvent casting and extrusion casting films is because the extruded films were cut and measured with the long dimension parallel to the extruding direction which considered orientation process for the films. The differences between annealed and unannealed samples in both processing methods are due to crystallinity increase which contributes to the toughness of the films.

These results of the mechanical properties are agreed well with others reported by Perego and Cella (2010) [104]
**Table 13**: Mechanical properties of PLA1 (solvent vs. extrusion)

<table>
<thead>
<tr>
<th>Processing method</th>
<th>Solvent Casting</th>
<th>Extrusion Casting</th>
<th>Perego and Cella (2010)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PLA1</td>
<td>PLA1 annealed</td>
<td>PLA1</td>
</tr>
<tr>
<td><strong>Samples name</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PLA1</td>
<td>49.6</td>
<td>56.3</td>
<td>43.5</td>
</tr>
<tr>
<td>PLA1 annealed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Tensile Properties</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak Stress MPa</td>
<td>2.9</td>
<td>2.6</td>
<td>3.6</td>
</tr>
<tr>
<td>Elongation %</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Modulus MPa</td>
<td>3038.4</td>
<td>3096.1</td>
<td>2911.7</td>
</tr>
</tbody>
</table>
Part II

5.11 Result of Solvent vs. Extrusion Casting (comparison)

5.11.1 Release study result
Result of solvent vs. extrusion casting release profile is shown in Figure 62. The left graph shows the release kinetics of tocopherol from solvent casting film, while the right graph shows the result of the extruded film. The trends of the release profile are similar though the amount of tocopherol release is far different. Release from solvent casting film shows 90% of tocopherol was released in 35 hours and release of tocopherol from extrusion casting shows only 40% of tocopherol released within same time. However, the results of the annealed film are almost identical 10-11% released in 35 hour. The reason for this is because they share similar amount of crystallinity content, while the unannealed film showed different release due to different amount in crystallinity contents. It is clear that the method of producing the films have significant effects on the release profile of tocopherol and the data from solvent casting cannot be translated to represent the extrusion directly.
5.11.2 SEM result

When compare the resulted films from the two methods and as appear in Figure 63, the first row is depicting the SEM images of solvent casting method which shows the solvent evaporation effects due to partial pressure of chloroform. The second row shows the resulted films from extrusion and here the rolls created this homogenous surface morphology. Though the differences is clear between the two morphologies at this point we are not interested in looking into the details since we are more interested the results of release profile and mechanical properties in this phase of study.
Figure 63: Solvent vs. extrusion SEM images
5.11.3 Crystallinity result

The result shows more than 40% crystallinity in the extruded films while the solvent casting film shows around 20% crystallinity.

Obviously, extrusion casting creates more crystalline content almost double of the solvent casting Figure 63. The reason behind this huge difference in crystallinity content is due to shear and orientation in the extruder which apparently create more crystals.

![Figure 64: Crystallinity % of film produced by solvent and extrusion casting](image-url)
6 CONCLUSIONS

Conclusion Part I

The changes in stereochemical isomer and processing conditions of PLA films have shown significant effects on the release profile and diffusivity of tocopherol. They appeared to be the controlling factors of the final properties of CRP films to achieve different release profiles.

The effects of stereochemical isomer of PLA was demonstrated by providing different release profiles of tocopherol and the range was covered from 100% (immediate release) to 80% in 58 hours in the pure PLA and its different blends. Annealing of the pure PLA and its different blends increased crystallinity content (38-53%) hence decrease the amount of tocopherol released to 30% in 58 hours by hindering the migration of tocopherol through the polymer matrix.

The stereochemical isomer of the commercial PLA grade (PLA1 and PLA2) also showed different release amount of tocopherol extent from 5 to 100% in the first 8 hours. The processing conditions (drying and annealing) made additional changes in crystallinity of PLA1 and PLA2 and decreased the release amount of tocopherol significantly. The combinational effects of stereochemical isomer and processing conditions can be seen clearly in increase of crystallinity and extension the ranges of tocopherol release profiles.

The Fickian model fitted well with the experimental data and the diffusion coefficients were estimated between $2.42\times10^{-19}$ to $8.68\times10^{-16}$ m$^2$/s with three orders of magnitude. This varied range of tocopherol diffusivities, based on initial amount loaded (3000 ppm),
was achieved from PLA taking advantages of its ability to undergo main-chain segmental motion and the amorphous and crystalline phase changes during the processing. Although the three orders of magnitude of diffusivity were achieved, the cover of this range to prolong the induction period in lipid oxidation reaction remains unknown, since other factors such as initial tocopherol loading amount and package design have to be considered. The result also indicates that the transformation of PLA-CRP films during the course of annealing reduces the release of tocopherol due to the formation of more crystalline in the film matrix.

Annealing process increased film crystallinity, which led to slower tocopherol release and lower diffusivity. It also decreased water vapor transmission rate (by half) and oxygen transmission rate of the films (by 3 to 4 times).

Regardless of the processing method, result show more than 95% of tocopherol has been recovered (total extraction) from all film samples, indicating that there was less lost during the course of producing and annealing of the CRP films. This result was expected based on the PLA and tocopherol molecular structures where there is only physical entrapment and nonexistence of chemical interactions or bonding of any kind. Tocopherol is a nonvolatile compound and stable at the level of PLA extrusion temperature, which eliminates any possibility of loss due to evaporation or degradation during the process of films production. Total extraction was also an indication of the well incorporation of tocopherol into PLA matrix.

**Conclusion Part II**

The films produced by solvent casting and extrusion casting showed completely different
tocopherol release properties, albeit sharing the same profile trend. Release profile result of solvent casting was more than double of extrusion casting. Though the tocopherol release profiles were found to be different in both processing methods, surprisingly, the tocopherol release profiles of annealed films from both methods were almost matching.

The annealing process increased crystallinity in the films, which slowed down tocopherol release. Data from both processing methods were only comparable in terms of mechanical properties i.e. tensile strength and elastic modulus, which is in agreement with data mentioned in the literature. This result suggests that release profile data of solvent casting cannot be used to infer directly to extrusion casting release profile data.

The scanning electron microscopy revealed distinctive topographies between films produced by the two methods. In solvent casting method, the evaporation process shaped a rough surface morphology, while in extrusion casting the rolls created a consistent smooth surface morphology. This might be an indication of differences in crystal type, shape and size between the films produced by these two methods, which in return affected their tocopherol release kinetics. Due to differences in PLA morphology and release behavior obtained from using solvent and extrusion casting methods, solvent casting method is not a viable approach for PLA data interpretation if intended for CRP applications. Further work is needed to extrapolate data from solvent to extrusion casting in terms of release properties from commercial point of view.

In summary, PLA shows potential of being tailored, through control of stereochemical isomer and manipulation of processing conditions, to accommodate different CRP applications. It is possible to exploit this behavior of PLA to obtain a wide range of diffusion of different active compounds for the use of varied food applications.
7 FUTURE WORK

7.1 Study the crystallinity effect on tocopherol release profile

Based on our finding in this study that the crystallinity plays a major role in the release kinetics of PLA film, investigate the crystallinity effect is a crucial step to understand how it hinder the diffusion of tocopherol through PLA matrix.

Another aspect needed to be addressed is the molecular weight of PLA and its effect on the release kinetics of tocopherol since it affect PLA mechanical properties and crystallization behavior. The molecular weight and stereochemical are the makeup of the PLA backbone. The stereochemical makeup is easy to control by polymerization with D-lactide, L-lactide, D, L-lactide, or meso-lactide to form random or block stereocopolymers, while the molecular weight is directly controlled by the addition of hydroxylic compounds, such as lactic acid, water, alcohols.

Study the 3D network structure of the blend of L and D in crystalline region and how it hinder the diffusion of tocopherol through its structure plus the effect of the thickness of the film on tocopherol release profile.

7.2 Extrapolate the data from solvent to extrusion casting

Establish relationships between L and D ratios, crystallinity % and release profiles of tocopherol using mathematical modeling. For instant knowing the type, shape, size, and percentage of crystals in the polymer matrix will provide detailed information on how the migration of tocopherol happens. These data from films made using both methods solvent and extrusion casting will help in establishing a correlation to understand the release
kinetics of each film.

### 7.3 Use of real food system

Use real food system to study the real meaning of the wide range of tocopherol release profiles and diffusivities. The ultimate goal is to drive some correlation between diffusivity and shelf life of food as illustrated in Figure 65. The diagram is a vision of how to apply the result of shelf life and diffusivity study, e.g. produce different films with different diffusivities and each one of them link it with specific shelf life for specific food product.

![Figure 65: Shelf life and diffusivity relationship](image-url)
8 REFERENCES


60. Suryanegara, L., A.N. Nakagaito, and H. Yano, *The effect of crystallization of PLA on the thermal and mechanical properties of microfibrillated cellulose-


