

**CONTINUOUS BLENDING APPROACH IN THE MANUFACTURE OF  
EPOXIDIZED SOYBEAN-PLASTICIZED POLY(LACTIC ACID) SHEETS AND  
FILMS FOR PACKAGING APPLICATIONS**

**By**

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## **ABSTRACT**

### **CONTINUOUS BLENDING APPROACH IN THE MANUFACTURE OF EPOXIDIZED SOYBEAN-PLASTICIZED POLY(LACTIC ACID) SHEETS AND FILMS FOR PACKAGING APPLICATIONS**

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A single-step processing system in which an extruder and a peristaltic injector pump attached in tandem was developed for a continuous and accurate incorporation of epoxidized soybean oil (ESO) into poly (lactic acid) (PLA) matrix in order to manufacture sheet/film with improved flexibility and toughness. The impact strength of plasticized sheets increased significantly with increasing ESO content, indicative of the toughening capacity of ESO as a plasticizer. The ductility of plasticized PLA sheets followed similar trends and the brittle-to-ductile transition occurred in the range of 5-10 wt % ESO content, in agreement with the impact strength results. In contrast, both the tensile strength and the modulus of the sheets decreased with increasing ESO content due to the plasticization effect, which induced a decrease in the glass transition temperature. Burst pressure and seal strength of PLA films were not affected by the addition of plasticizer or by the sealing temperature range studied. The tensile properties of blown film plasticized with 15 wt % ESO, tested at periodic intervals of storage time, indicated no significant change in the ductility and the tensile strength at yield as the storage time increased, implying the good permanence of ESO in the plasticized PLA films. In contrast, the tensile modulus showed a slight but a statistically significant increase in stiffness after only 7 storage days, indicating a possible loss of plasticizer from the film as the storage time increased. This contradictory trend will be investigated further.

**Dedicated to my parents**  
**Vijayarajan and Bhuvaneswari**

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## TABLE OF CONTENTS

|   |     |
|---|-----|
| LIST OF TABLES .....                            | vii |
| LIST OF FIGURES .....                           | x   |
| Chapter 1                                       |     |
| INTRODUCTION .....                              | 1   |
| 1.1 Introduction .....                          | 1   |
| 1.2 Objectives .....                            | 7   |
| 1.3 Structure of thesis .....                   | 7   |
| 1.4 References .....                            | 10  |
| Chapter 2                                       |     |
| BACKGROUND AND LITERATURE REVIEW .....          | 12  |
| 2.1 Introduction .....                          | 12  |
| 2.2 Poly (lactic acid) .....                    | 12  |
| 2.2.1 Synthesis of PLA .....                    | 12  |
| 2.2.2 Properties of PLA .....                   | 14  |
| 2.2.3 Property modification of PLA .....        | 17  |
| 2.2.3.1 Copolymerization .....                  | 17  |
| 2.2.3.2 Melt blending with other polymers ..... | 18  |
| 2.2.3.3 Plasticization .....                    | 19  |
| 2.3 Soybean oils .....                          | 20  |
| 2.3.1 Synthesis of ESO .....                    | 21  |
| 2.3.2 Use of ESO as a plasticizer .....         | 23  |
| 2.4 Processing technologies of PLA .....        | 24  |
| 2.4.1 Drying and extrusion .....                | 24  |
| 2.4.2 Injection molding .....                   | 25  |
| 2.4.3 Stretch blow molding .....                | 25  |
| 2.4.4 Thermoforming .....                       | 26  |
| 2.4.5 Cast film and sheet .....                 | 26  |
| 2.4.6 Extrusion blown film .....                | 27  |
| 2.5 References .....                            | 29  |
| Chapter 3                                       |     |
| EXPERIMENTAL .....                              | 33  |
| 3.1 Materials .....                             | 33  |
| 3.2 Sample manufacturing .....                  | 34  |
| 3.2.1 Manufacture of plasticized sheets .....   | 34  |
| 3.2.2 Manufacture of plasticized films .....    | 38  |
| 3.3 Property evaluation .....                   | 39  |

|   |    |
|---|----|
| 3.3.1 Mechanical properties .....       | 39 |
| 3.3.2 Thermal property .....            | 41 |
| 3.3.3 Phase morphology evaluation ..... | 42 |
| 3.3.4. Statistical analysis .....       | 42 |
| 3.4 References .....                    | 44 |

#### Chapter 4

|   |    |
|---|----|
| RESULTS AND DISCUSSION .....  | 45 |
| 4.1 Effect of ESO content on the notched Izod impact strength of PLA sheets ..... | 45 |
| 4.2 Effect of ESO content on the tensile properties of PLA sheets .....           | 48 |
| 4.2.1. Ductility .....  | 48 |
| 4.2.2. Tensile Strength and Modulus .....   | 53 |
| 4.3 Effect of ESO on package related properties .....                             | 55 |
| 4.3.1 Burst pressure of PLA films .....   | 55 |
| 4.3.2 Seal strength of PLA films .....  | 56 |
| 4.3.3 Tensile properties of plasticized films as a function of storage time ..... | 57 |
| 4.4 References .....  | 60 |

#### Chapter 5

|                       |    |
|-----------------------|----|
| CONCLUSIONS .....     | 61 |
| 5.1 Conclusions ..... | 61 |
| 5.2 Future work ..... | 63 |
| 5.3 References .....  | 65 |

#### APPENDICES

|  |    |
|--|----|
| APPENDIX I - IMPACT STRENGTH DATA OF PLA SHEETS .....  | 67 |
| APPENDIX II - TENSILE PROPERTIES DATA OF PLA SHEETS .....  | 70 |
| APPENDIX II-1 - The Effect of ESO Content on the Tensile Modulus of PLA Sheets .....   | 71 |
| APPENDIX II-2 - The Effect of ESO Content on the Tensile Strength at Yield of PLA Sheets .....                               | 74 |
| APPENDIX II-3 - The Effect of ESO Content on the Ductility of PLA Sheets .....   | 77 |
| APPENDIX III - TENSILE PROPERTIES DATA OF PLA FILMS .....  | 81 |
| APPENDIX III-1 - The Effect of Storage Time on the Tensile Strength at Yield of PLA Films Plasticized with 15 wt % ESO ..... | 82 |
| APPENDIX III-2 - The Effect of Storage Time on the Tensile Modulus of PLA Films Plasticized with 15 wt % ESO .....           | 85 |
| APPENDIX III-3 - The Effect of Storage Time on the Energy to Break of PLA Films Plasticized with 15 wt % ESO .....           | 88 |
| APPENDIX III-4 - The Effect of Storage Time on the Ductility of PLA Films Plasticized with 15 wt % ESO .....                 | 91 |
| APPENDIX IV - BURST PRESSURE AND SEAL STRENGTH DATA OF PLA FILMS .....   | 95 |

|   |    |
|---|----|
| APPENDIX IV-1 - Effect of Sealing Temperature on the Burst Pressure of PLA<br>Films ..... | 96 |
| APPENDIX IV-2 - Effect of Sealing Temperature on the Seal Strength of PLA Films           | 99 |

## LIST OF TABLES

|            |   |    |
|------------|---|----|
| Table 2.1  | Comparison of PLA properties with other petroleum based polymers .....  | 16 |
| Table 3.1  | Characteristics of PLA (2002D) resin used in this study .....   | 33 |
| Table 4.1  | Effect of ESO content on the glass transition ( $T_g$ ) of PLA (2002D)<br>measured by DSC and DMA .....                                 | 54 |
| Table 4.2  | Effect of sealing temperature on the burst pressure and sealing strength of<br>unplasticized (neat) PLA and plasticized PLA films ..... | 56 |
| Table 4.3  | Variations in tensile properties of plasticized PLA films as a function of<br>storage time .....  | 58 |
| Table A.1  | Effect of ESO content on the impact strength of PLA sheets .....  | 68 |
| Table A.2  | Analysis of variance for the effect of ESO content on the impact strength<br>of PLA.....  | 69 |
| Table A.3  | Pairwise comparison of impact strength of PLA/ESO blends .....  | 69 |
| Table A.4  | Effect of ESO content on the tensile modulus of PLA sheets .....  | 72 |
| Table A.5  | Analysis of variance for the effect of ESO content on the tensile modulus<br>of PLA.....  | 73 |
| Table A.6  | Pairwise comparison of tensile modulus of PLA/ESO blends .....  | 73 |
| Table A.7  | Effect of ESO content on the tensile strength at yield of PLA sheets .....  | 75 |
| Table A.8  | Analysis of variance for the effect of ESO content on the tensile strength<br>at yield of PLA.....                                      | 76 |
| Table A.9  | Pairwise comparison of tensile strength at yield of PLA .....   | 76 |
| Table A.10 | Effect of ESO content on the tensile strain at break and at yield of PLA<br>sheets.....   | 78 |
| Table A.11 | Effect of ESO content on the ductility of PLA sheets.....   | 79 |
| Table A.12 | Analysis of variance for the effect of ESO content on the ductility of PLA.....   | 80 |
| Table A.13 | Pairwise comparison of ductility of PLA/ESO blends .....  | 80 |



|  |     |
|--|-----|
| Table A.14 Effect of storage time on the tensile strength at yield of plasticized PLA films .....                              | 83  |
| Table A.15 Analysis of variance for the effect of storage time on the tensile strength at yield of plasticized PLA films ..... | 84  |
| Table A.16 Pairwise comparison of tensile strength at yield of plasticized PLA films .....                                     | 84  |
| Table A.17 Effect of storage time on the tensile modulus of plasticized PLA films .....  | 86  |
| Table A.18 Analysis of variance for the effect of storage time on the tensile modulus of plasticized PLA films .....           | 87  |
| Table A.19 Pairwise comparison of tensile modulus of plasticized PLA film .....  | 87  |
| Table A.20 Effect of storage time on the energy at break of plasticized films .....  | 89  |
| Table A.21 Analysis of variance for the effect of storage time on the energy at break of plasticized PLA film .....            | 90  |
| Table A.22 Pairwise comparison of energy at break of plasticized PLA film .....  | 90  |
| Table A.23 Effect of storage time on the tensile strain at break and at yield of plasticized films .....                       | 92  |
| Table A.24 Effect of storage time on the ductility of plasticized films .....  | 93  |
| Table A.25 Analysis of variance for the effect of storage time on the ductility of plasticized PLA films .....                 | 94  |
| Table A.26 Pairwise comparison of ductility of plasticized PLA films .....   | 94  |
| Table A.27 Effect of sealing temperature on the burst pressure of unplasticized and plasticized films .....                    | 97  |
| Table A.28 Analysis of Variance for the effect of sealing temperature and plasticization on the burst pressure PLA films ..... | 98  |
| Table A.29 Pairwise comparison of burst pressure of PLA films .....  | 98  |
| Table A.30 Effect of sealing temperature on the seal strength of unplasticized films .....                                     | 100 |
| Table A.31 Effect of sealing temperature on the seal strength of plasticized films .....                                       | 101 |
| Table A.32 Analysis of variance for the effect of sealing temperature and plasticization on the seal strength PLA films .....  | 102 |

|  |     |
|--|-----|
| Table A.33 Pairwise comparison of seal strength of PLA films ..... | 102 |
|--|-----|

## LIST OF FIGURES

|            |   |    |
|------------|---|----|
| Figure 2.1 | Chemical structures of L-lactic acid and D-lactic acid .....  | 13 |
| Figure 2.2 | Chemical structures of LL-lactide, meso or LD-lactide and DD-lactide .....  | 14 |
| Figure 2.3 | Schematic representation of triglyceride structure in vegetable oils .....  | 21 |
| Figure 2.4 | Structure of epoxidised soy oil (ESO) .....   | 22 |
| Figure 3.1 | The schematic representation of the tandem extrusion-injection pump system used in this study .....   | 35 |
| Figure 3.2 | Calibration curve for determining the amount of extruded PLA in the blends .....  | 36 |
| Figure 3.3 | Calibration curve for determining the amount of ESO injected in the blends .....  | 37 |
| Figure 4.1 | Effect of ESO content on the impact strength of PLA .....   | 45 |
| Figure 4.2 | SEM micrographs of PLA plasticized with various amounts of ESO: (a) 0 wt %, (b) 10 wt %, and (c) 20 wt % .....  | 47 |
| Figure 4.3 | Stress-strain curves of (a) Unplasticized PLA and PLA plasticized with various amounts of ESO showing well defined yield points and (b) Plasticized PLA showing stable necking beyond yield point ..... | 49 |
| Figure 4.4 | Tensile deformation showing the stress whitening in unplasticized PLA (left) and PLA plasticized with 10 wt % ESO (right) .....   | 50 |
| Figure 4.5 | Effect of ESO content on the ductility of the PLA sheet .....   | 52 |
| Figure 4.6 | Effect of ESO content on the tensile stress at yield and tensile modulus of PLA sheets .....  | 54 |

## **Chapter 1**

### **INTRODUCTION**

#### **1.1 Introduction**

Petroleum-based polymers have served mankind in numerous ways and are widely used in many applications in the United States. However, the continued increase in oil prices, U.S. dependency on foreign oil and environmental concerns has led to a growing interest in bio-based plastics [1]. Replacing petroleum-based polymers with natural bio-based polymers obtained from renewable resources, which can be biodegraded, could be an attractive alternative for a sustainable environment [2, 3].

The most common biodegradable polymers are the aliphatic polyesters such as polylactic acid (PLA), polyglycolic acids (PGA), polycaprolactone (PCL) and polyhydroxybutyrate (PHB). Among these polymers, PLA obtained from corn and sugar beets is commercially gaining a lot of interest recently. PLA has attracted the interest of many researchers as it has relatively high modulus, reasonable strength, thermal plasticity, excellent flavor and aroma barrier capability, good heat sealability and easy processing, thereby making it one of the most promising bio-based polymers [4, 5]. It possesses properties that are equivalent or better than many petroleum-based plastics; for instance it has the stiffness and tensile strength of polyethylene terephthalate and processing characteristics of polystyrene [6].

Despite these attractive properties, PLA has few commercial applications concentrating mainly in textile and specialty biomedical niches such as sutures and drug delivery devices due to its bio-degradability and bio-compatibility [6, 7]. Additionally, it is being used as a commodity polymer for packaging food and consumer goods where the

physical properties of PLA make it suitable for manufacture of rigid containers and bottles. However, the widespread applicability of PLA in flexible sheets and films is limited because of its brittleness, lower impact resistance at room temperature and narrow processing windows [5-8]. These factors severely hinder its applicability, particularly in packaging applications where production lines for flexible films cannot tolerate film cracking or tearing when folded or subjected to force during manufacturing [1]. Processing of PLA in thermoforming and film blowing production lines is still difficult due to its low melt strength [9-12]. Therefore, it is of paramount importance to find a tougher and ductile variant of the polymer in order to overcome these difficulties and broaden the range of its commercial applications [6].

In order to improve the properties of PLA, it is often blended or copolymerized with other materials [9-12]. The compatibility of the two components in the blend affects the properties such as glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ), crystallinity, and morphology. Consequently, these properties determine the properties of the macroscopic material such as processability, rigidity, impact and tensile strength, barrier properties and degradation. Blending is more cost-effective than copolymerization and hence more frequently used method [11]. PLA is most commonly blended with a second polymer or with plasticizers [9-12].

Blending of PLA with a biodegradable second polymer such as poly(vinyl alcohol), poly(caprolactone), poly(ethylene glycol), poly(hydroxyalkanoate), and poly(butylene succinate) has predominantly been used in biomedical applications to maintain the bio-compatibility and biodegradability while also improving the mechanical properties [8]. For example, significant improvement in flexibility (up to 180%

elongation at break compared to 4% for neat PLA) and impact resistance (over 200% increase) were obtained with the use of up to 10 wt % low molecular weight poly(ethylene-glycol) (PEG) [9]. However, these additives are relatively exorbitant rendering their PLA blends expensive. Alternatively, the use of inexpensive non-biodegradable polymers such as poly(ethylene oxide), poly(vinyl acetate), polyisopropene, acrylonitrile/butadiene/styrene copolymer, and polyethylene has successfully reduced cost. The PLA blends with these polymers require an additional component such as a compatibilizer to improve the miscibility of the blend [8]. Eliminating the use of compatibilizer, a study by other investigators focused on the use of petroleum-based ethylene/acrylate copolymer (EAC), which is compatible and miscible with PLA, to improve the impact and tensile properties of PLA [8].

Alternatively, the use of plasticizers such as low molecular weight esters, oligomeric lactic acid, etc., has been investigated to obtain PLA with improved mechanical properties without the addition of a compatibilizer [9, 10]. In the case of semicrystalline polymers like PLA, an efficient plasticizer reduces the glass transition temperature ( $T_g$ ) thereby increasing the flexibility to overcome the difficulties of cracking or tearing, especially in packaging film production lines [10].

PLA film has been gaining a lot of attention in flexible packaging applications and many studies have been conducted to characterize and understand the physical, mechanical and barrier properties of the film [11,13]. Investigations of PLA blended with monomeric and oligomeric plasticizers such as citrates and PEG resulted in films with enhanced flexibility and thereby reduced brittleness [11]. Coating PLA films with  $\text{SiO}_x$ , an anti UV layer and varnish has been shown to improve the physical, mechanical and

barrier properties of the films for food packaging applications [13]. Transparent films with enhanced mechanical properties have also been produced using PLA plasticized with adipates [7].

Although blending PLA with the aforementioned plasticizers improves its properties and may broaden its applications, the majority of these plasticizers are derivatives of crude oil and non-biodegradable [14]. Hence, it is essential to blend PLA with renewable and biodegradable plasticizers that could withstand the practical application while their biodegradation properties are maintained [12].

Recently, modified vegetable oils have gained a lot of interest as a renewable source of plasticizer for polymers [14]. Soybean oil (SO) is one such renewable material that has been investigated as a plasticizer for PLA, poly(vinyl chloride) (PVC), polybutylene succinate (PBS), etc. [15]. Soy oil is a mixture of triglycerides with various saturated and unsaturated fatty acids [16]. Epoxidation of the unsaturated bonds that occur along with the fatty acid chains produces more reactive oxirane groups. This three-member ring provides a more energetically favorable site for reaction and represents a chemical intermediate [17]. Epoxidized soy oil (ESO) is prepared on an industrial scale and is being used for polymers, coatings, adhesives, laminate materials, etc. [17]. Currently, research studies are directed towards the use of ESO as a plasticizer for both non-biodegradable and biodegradable polymers [16].

In relation to non-biodegradable polymers, such as PVC compounds, phenolic resins, and chlorinated rubbers, ESO has been used as a non-toxic plasticizer to improve the polymer stability and flexibility [16]. Studies on the effect of ESO on polyvinyl chloride/epoxidized natural rubber thermoplastic elastomer (PVC/ENR) indicate that

ESO-plasticized blends exhibit good tear strength, good tensile strength and lower  $T_g$  [18]. Investigation on phenolic resins plasticized with ESO prepared for laminate materials has shown not only increased flexibility of the phenolic resins but also improved electrical properties, solvent resistance, and heat resistance of the laminates [19].

Biodegradable polymers such as poly(3-hydroxybutyrate-co-3 hydroxyvalerate) (PHBV) and PLA have been plasticized with ESO [20-22]. PHBV plasticized with ESO resulted in reduced  $T_g$  as well as increased elongation at break and impact strength [20, 21]. Other investigations have shown that the addition of ESO into PLA lowers the  $T_g$ , storage modulus, and viscosity of the blend while improving the elongation at break [17, 22]. Higher melt strength was obtained by adding higher ESO content into PLA, resulting in higher elongation of the blend [17].

Although ESO has been reported as an effective plasticizer for bio-degradable polymers due to its excellent permanency and efficiency of plasticization [16], the research conducted so far on PLA plasticized with ESO has mostly focused on the effect of plasticizer types and/or addition levels on the mechanical properties without due consideration of the production methods for these blends.

Several multi-step approaches to formulating PLA/ESO blends have been investigated [10, 14]. In most studies ESO is pre-mixed with PLA prior to shaping the blend in an extruder or using other processing techniques [17]. Melt blending of PLA with ESO in an internal mixer prior to compression molding of the blend in a hot press has also been reported [22]. Another reported approach for using EPO as a PLA



plasticizer consists of first dissolving each material in a chloroform solution and subsequently mixing the two solutions to obtain a blended mixture, which was then dried to form sample pellets for further processing [23].

The above described processes involve multiple steps, including pre-blending PLA and ESO in a batch mixer prior to film production in another processing system [10, 14]. In these multi-step approaches, the resultant PLA polymer is subjected to repetitive cycles of high processing temperature, which could affect the miscibility of PLA and ESO and also the phase separation between the two at different composition levels. This multi-step approach could be efficient at the research laboratory level for small scale production of the blends. However, the multiple steps involved in the production of flexible films make such a process both time consuming and very energy intensive, thus preventing its scalability. A more efficient and effective technique is required that avoids the additional step of pre-mixing before extrusion.

The main goal of this study is to take the next step to manufacture flexible PLA films using a novel one step-process. It is believed that the elimination of the pre-blending steps will reduce the processing energy, and therefore will lead to a cost-effective process for the production of fully biodegradable flexible PLA films to be used in sustainable packaging applications. This study will explore the feasibility of a continuous method of blending ESO and PLA needed for the manufacture of flexible PLA sheet and film.

## **1.2 Objectives**

The goal of this study is to develop a single-step process that efficiently incorporates ESO into a PLA matrix in order to manufacture PLA sheet/film with improved ductility, flexibility and impact resistance. To achieve this aim, the following specific objectives must be accomplished:

1. Explore the feasibility of a novel single-step method that continuously introduces a metered amount of ESO into the PLA matrix, thereby eliminating the intermediate step of mixing the polymer and plasticizer prior to extrusion.
2. Evaluate the effect of different concentrations of ESO on the impact strength, ductility and other tensile properties of plasticized PLA with the ultimate goal of identifying the brittle to ductile transition in the PLA/ESO blend.
3. Examine the miscibility and phase morphology of the PLA/ESO blends to gain an in-depth understanding of the interactions between PLA and ESO.
4. Manufacture PLA/ESO films by varying the amounts of ESO in the films and characterize their physico-mechanical properties.
5. Characterize the properties of the plasticized films as a function of time in order to determine the permanence or leachability of the plasticizer in the films.

## **1.3 Structure of thesis**

This thesis is structured as follows: the first chapter introduces the rationale of this research. Background on polylactic acid, ESO and their blending techniques is reviewed in Chapter 2. The experimental details, including the material specifications, property testing methods and equipment are discussed in Chapter 3. The results of the

effect of ESO addition levels and storage time on the different properties of plasticized PLA are discussed in Chapter 4. Conclusions drawn from experimental data and recommendations for future work are given in Chapter 5.

## **REFERENCES**

## 1.4 References

1. Matuana, L.M., Solid state microcellular foamed poly(lactic acid): Morphology and property characterization, *Bioresource Technology*, 99: 3643- 3650 (2008).
2. Haq, M., Burgueno, R., Mohanty, A.K., and Misra, M., Hybrid bio-based composites from blends of unsaturated polyester and soybean oil reinforced with nanoclay and natural fibers, *Composites Science and Technology*, 68: 3344-3351 (2008).
3. Wool, R.P and Sun, X.S., Bio-Based Polymers and Composites, Elsevier Inc., edition 1, pp 56-111 (2005).
4. Lee, S.Y., Kang, I.A., Doh, G.H., Yoon, H.G., Park, B.D. and Wu, Q., Thermal and mechanical properties of wood flour/talc-filled polylactic acid composites: effect of filler content and coupling treatment, *Journal of Thermoplastic Composite Materials*, 21 (3): 209-223 (2008).
5. Pilla, S., Gong, S., O'Neill, E., Rowell, R.M., and Krzysik, A.M., Polylactide-pine wood flour composites, *Polymer Engineering and Science*, 48: 578-587 (2008).
6. Schreck, K.M. and Hillmyer, M.A., Block copolymers and melt blends of polylactide with Nodax™ microbial polyesters: preparation and mechanical properties, *Journal of Biotechnology*, 132: 287-295 (2007).
7. Martino, V.P., Jimenez, A., and Ruseckaite, R.A., Processing and characterization of poly(lactic acid) films plasticized with commercial adipates, *Journal of Applied Polymer Science*, 112: 2010-2018 (2009).
8. Afrifah, K.A., Matuana, L.M., Impact modification of polylactide with a biodegradable ethylene/acrylate copolymer, *Macromolecular Materials and Engineering*, 295: 802-811 (2010).
9. Jacobsen, S. and Fritz, H.G., Plasticizing polylactide - the effect of different plasticizers on the mechanical properties. *Polymer Engineering and Science*, 39, 1303-1310 (1999).
10. Baiardo, M., Frisoni, G., Scandola, M., Rimelen, M., Lips, D., Ruffieux, K. and Wintermantel, E., Thermal and mechanical properties of plasticized poly(L-lactic acid), *Journal of Applied Polymer Science*. 90: 1731-1738 (2003).
11. Ljungberg, N. and Wesslen, B., Preparation and properties of plasticized poly(lactic acid) films, *Biomacromolecules*, 6: 1789-1796 (2005).
12. Semba, T., Kitagawa, K., Ishiaku, U.S., and Hamada, H., The effect of crosslinking on the mechanical properties of polylactic acid/polycaprolactone blends, *Journal of Applied Polymer Science*, 101, 1816-1825 (2006).

13. Siracusa, V., Blanco, I., Romani, S., Tylewicz, U., Rocculi, P., and Rosa, M.D., Poly(lactic acid)-modified films for food packaging application: physical, mechanical, and barrier behavior, *Journal of Applied Polymer Science*, 125: E390-E401(2012).
14. Robertson, M.L., Chang, K., Gramlich, W.M., and Hillmyer, M.A., Toughening of polylactide with polymerized soybean oil, *Macromolecules*, 43: 1807-1814 (2010).
15. Gramlich, W.M., Robertson, M.L., and Hillmyer, M.A., Reactive compatibilization of poly(L-lactide) and conjugated soybean oil, *Macromolecules*, 43: 2313-2321 (2010).
16. Zhao, Y., Qu, J., Feng, Y., Wu, Z., Chen, F., and Tang, H., Mechanical and thermal properties of epoxidized soybean oil plasticized polybutylene succinate blends, *Polymers for Advanced Technologies*, 23: 632-638 (2012).
17. Xu, Y.Q., Qu, J.P., Mechanical and rheological properties of epoxidized soybean oil plasticized poly(lactic acid), *Journal of Applied Polymer Science*, 112: 3185-3191 (2009).
18. Ishiaku, U.S., Shaharum, A., Ismail, H., and Mohd Ishak, Z.A., The effect of an epoxidized plasticizer on the thermo-oxidative ageing of poly(vinyl chloride)/epoxidized natural rubber thermoplastic elastomers, *Polymer International*, 45: 83-91 (1998).
19. Konii, S., Yoshimura, Y., Nanaumi, K., Yasuzawa, K., Yoshida, T., and Shinko, T., Process for producing internally plasticized phenolic resins, US patent P4209429 (1980).
20. Choi, J.S. and Park, W.H., Effect of biodegradable plasticizers on thermal and mechanical properties of poly(3-hydroxybutyrate), *Polymer Testing*, 23: 455-460 (2004).
21. Choi, J.S. and Park, W.H., Thermal and mechanical properties of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) plasticized by biodegradable soybean oils, *Macromolecular Symposia*, 197: 65-76 (2003).
22. Ali, F., Chang, Y.W., Kang, S.C., and Yoon, J.Y., Thermal, mechanical and rheological properties of poly(lactic acid)/epoxidized soybean oil blends, *Polymer Bulletin* 62: 91-98 (2009).
23. Al-Mulla, E.J., Yunus, W.M., Ibrahim, N.A., and Rahman, M.Z., Properties of epoxidized palm oil plasticized polylactic acid, *Journal of Materials Science*, 45:1942-1946 (2010).

## **Chapter 2**

### **BACKGROUND AND LITERATURE REVIEW**

#### **2.1 Introduction**

Consistent with the scope of this study, a background and literature review on the current studies of epoxidized soybean oil (ESO) plasticized poly(lactic acid) (PLA) blends are presented in this chapter. The review focuses on the effects of ESO on the mechanical and thermal properties of PLA as well as on the manufacturing methods of the ESO plasticized PLA films.

#### **2.2 Poly (lactic acid)**

Poly(lactic acid) belongs to the family of aliphatic polyesters and is biodegradable, compostable, and biocompatible. It is a thermoplastic derived from 100% renewable resources such as corn and sugar beets for use primarily in industrial packaging or bio-absorbable medical devices [1]. In addition to being an environmental friendly polyester, it has excellent properties including relatively high modulus, high strength, excellent flavor and aroma barrier, good heat sealability, and easy fabrication using existing processing technology and techniques [2-4].

##### ***2.2.1 Synthesis of PLA***

The basic building block of PLA is lactic acid, which can be manufactured by carbohydrate fermentation or chemical synthesis [5]. Lactic acid (2-hydroxy propionic acid) is the simplest hydroxyl acid with an asymmetric carbon atom and exists in two optically active configurations, the L(+) and D(-) isomers (Figure 2.1). The L(+) isomer

is produced in humans and other mammals, while both the D(-)- and L(+)- isomers are produced in bacterial systems. The majority of lactic acid commercially produced today is by bacterial fermentation of carbohydrates using modified strains of the genus *Lactobacilli*, which are exclusively form lactic acid [6].

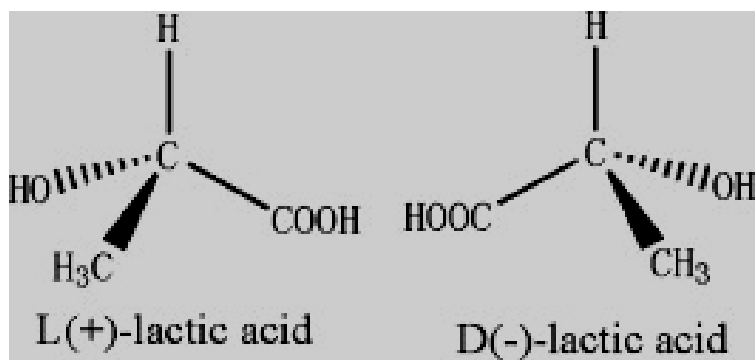


Figure 2.1: Chemical structure of L-lactic acid and D-lactic acid <sup>[7]</sup>

High molecular weight PLA can be produced using 3 different methods: (a) direct condensation polymerization, (b) azeotropic dehydration condensation, and (c) polymerization through lactide formation. Among these three methods, polymerization through lactide formation also called the ring opening polymerization of lactide, patented by Cargill Inc., is currently the most commonly used method for the production of PLA. In this method, lactide is formed by the condensation of two lactic acid molecules as follows: L- lactide (two L-lactic acid molecules), D- lactide (two D-lactic acid molecules) and meso-lactide (an L-lactic acid and a D-lactic acid molecule) (Figure 2.2) [5].



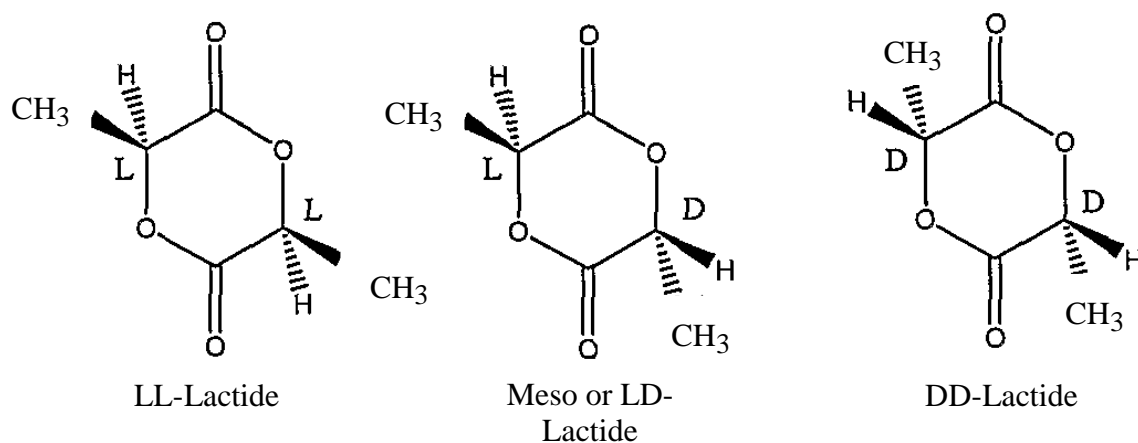


Figure 2.2: Chemical structures of LL-lactide, meso or LD-lactide and DD-lactide<sup>[8]</sup>

Many important properties of PLA are controlled by the type of lactide used and their sequence of arrangement in the polymers. For instance, the isotactic homopolymers (where the monomers in the chain are of the same optical composition): poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) are semicrystalline. However, random copolymers of L-, D-, and mesolactide result in amorphous PLAs [5]. Commercial PLAs are mostly blends of PLLA and PDLA or copolymer PDLLA obtained by the polymerization of LLA and DLLA [9]. PLA with 90% or more PLLA content tends to be crystalline while that with lower optical purity is amorphous [9].

### 2.2.2 Properties of PLA

Thermal properties such as glass transition temperature ( $T_g$ ), melting temperature ( $T_m$ ), and degree of crystallinity depend on various factors including the molecular weight, relative amounts of L- and D-lactic acid stereoisomers, thermal history, etc. Poly (L-lactic acid) (PLLA) and poly (D-lactic acid) (PDLA) made from L-lactide and D-lactide respectively, are semi crystalline polymers due to their stereoregularity. The

extent of crystallinity can be controlled by tuning the relative amounts of L- and D-lactic stereoisomers in the polymer. For instance, PLA containing more than 90% L-lactic acid is semicrystalline while lesser amounts of L-lactic acid, between 50% and 90%, will result in amorphous PLA. Most commercial grades of PLA are made of L-lactide with fewer amounts of Meso- and D-lactide [5].

Glass transition temperature and melting temperature can vary among different PLA types. In general, PLA has a glass transition temperature range between 40 and 70°C and a melting temperature between 130 and 180°C [10]. Thermal properties are also affected by the L-lactic acid content; higher L-lactic acid content increases the  $T_m$  and  $T_g$  [11].

PLA possesses good mechanical properties such as high tensile strength and high modulus when compared to other traditional plastics (Table 2.1). It also has lower impact resistance and lower strain at break than other petroleum based plastics. The impact strength increases with increasing molecular weight and crystallinity [5].

Table 2.1: Comparison of PLA properties with other petroleum based polymers<sup>[12, 13]</sup>

| Properties  | PLA    | PET  | PS   | HIPS | PP   |
|---|--------|------|------|------|------|
| T <sub>g</sub> (°C)   | 55     | 75   | 105  |      | -10  |
| Density (g/cc)  | 1.24   | 1.33 | 1.05 |      | 0.9  |
| Heat Capacity (BTU/lb. °F)  | 0.39   | 0.44 | 0.54 |      | 0.3  |
| Notched Izod (ft.lb/in)   | 0.24   | 2.6  | 0.5  | 2.3  | 2    |
| Gardner Impact (in.lb)  | 0.5    | 2.8  | 4.5  | 100  | 7    |
| Tensile Strength @ Break (psi)  | 7700   | 7900 | 6500 | 3300 | 4500 |
| Tensile Modulus (Kpsi)  | 500    | 400  | 420  | 300  | 130  |
| % Elongation  | 6      | 130  | 7    | 45   | 120  |
| Water vapor permeability<br>( $\times 10^{-3}$ ) (kg m/m <sup>2</sup> s Pa) | 80-360 | 110  | 670  |      | 225  |
| Cost \$US/lb  | 1.80   | 0.74 | 0.74 | 0.77 | 0.68 |

The barrier property of a polymer, which is the ability of a molecule to permeate through its membrane or be obstructed by it, is very critical in designing any package system. Barrier properties are generally characterized by parameters such as permeability, diffusivity, and solubility coefficients [14]. PLA is a good barrier to carbon dioxide but is a poor barrier to oxygen and water vapor. PLA has a CO<sub>2</sub> permeation coefficient of  $1.76 \times 10^{-17}$  kg·m/m<sup>2</sup>·s·Pa and oxygen permeation coefficient of  $3.3 \times 10^{-17}$  kg·m/m<sup>2</sup>·s·Pa [15].

### ***2.2.3 Property modification of PLA***

Properties of PLA can be modified in different ways such as by copolymerization, blending with other resins, plasticization, etc. Modification is performed to obtain improved material properties compared to the neat PLA so that the material becomes suitable for a specific application.

#### ***2.2.3.1 Copolymerization***

Copolymerization is a method by which two or more monomers are combined into one polymeric chain to achieve specific properties. The mechanical properties of copolymerized PLA have been extensively investigated for various packaging applications.

Copolymerization of PLA can be conducted through polycondensation of lactic acid with other monomers. However, ring opening copolymerization of lactide with other cyclic monomers is widely preferred because of the precise control of the chemistry and the higher molecular weight of the copolymers produced. Depending on the different

molecular architecture of the copolymers they can be classified as random, block, graft or cross-linked copolymers [16].

Monomers that have been copolymerized with lactic acid include glycolide derivatives, lactones, cyclic amide esters, cyclic ether esters, and cyclic carbonates. For example, poly(lactic-glycolic acid), a copolymer of lactic acid and glycolic acid, is approved by the Food and Drug Administration (FDA) for clinical uses [17]. Although these copolymerized PLAs have a wide range of mechanical properties; they are not economically viable or cannot be produced in a large scale for packaging applications [18].

#### *2.2.3.2 Melt blending with other polymers*

Melt blending of existing polymers is considered a more economical and convenient method to achieve specific properties than synthesizing new polymers. PLA has been blended with various polymers for different purposes [16]. Blending of PLA with rubbery polymers has been predominantly emphasized in biomedical applications, resulting in the use of biodegradable and biocompatible polymers such as poly(vinyl alcohol), poly( $\epsilon$ -caprolactone), poly(ethylene glycol), polyhydroxyalkanoate, and poly(butylene succinate) as the second polymer phase [19].

The impact strength of PLA can considerably be improved by direct mechanical blending with inexpensive non-degradable polymers such as poly(ethylene oxide), poly(vinyl acetate), polyisoprene, acrylonitrile-butadiene-styrene copolymer and polyethylene. However, the majority of these modifiers are also thermodynamically immiscible with PLA and lack favorable interactions due to differences in their chemical

structures which results in weak interfacial adhesion (indicated by poor dispersion, very broad size distribution and distinct particle interfaces) and poor mechanical properties. Compatibilizers are therefore required to improve the interaction between PLA and the other polymers in order to improve the properties of the blend [20]. For instance, significant improvement in the impact strength and impact fracture toughness was reported for PLA/polycaprolactone (PCL) blends compatibilized with dicumyl peroxide and lysine triisocyanate [16]. However, a recently reported study eliminated the need for compatibilizer by using ethylene/acrylate copolymer (EAC), a petroleum-based impact modifier which is compatible with PLA. It was found that melt blending PLA with EAC improved the mechanical properties of the PLA while also maintaining its biodegradability at low concentrations [20].

#### *2.2.3.3 Plasticization*

The brittleness and lower impact resistance of PLA greatly limit its applicability in the packaging industry. In packaging applications, films are required to be flexible because industrial production lines cannot tolerate film cracking or tearing when folded or subjected to force during manufacturing [21]. Softening of PLA with plasticizers increases the flexibility and toughness of the produced films. In general, the plasticizers used with PLA should have the following characteristics: non-toxic, miscible, not prone to migration, not volatile and biodegradable [22]. Usually the introduction of a plasticizer into a plastic decreases its glass transition temperature ( $T_g$ ) while increasing the flexibility of the polymer chains, which in turn lowers the tensile strength and modulus of the plastic.

Ljungber and Wesslèn studied triacetine, tributyl citrate, acetyl tributyl citrate, triethyl citrate, and acetyl triethyl citrate and their plasticizing effect on PLA through dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) and observed significant reduction in the  $T_g$  [22]. Investigations of PLA blended with monomeric and oligomeric plasticizers such as citrates and PEG resulted in films with enhanced flexibility and thereby reduced brittleness [23]. Transparent films with enhanced mechanical properties have been produced from PLA plasticized with adipates [24].

Although plasticizing PLA with the aforementioned plasticizers improves its properties and may broaden its applications, the majority of these plasticizers are derivatives of crude oil and are non-biodegradable [25]. Hence, it is essential to blend PLA with renewable and biodegradable plasticizers that could withstand the practical application while their bio-degradation properties are maintained. Epoxidized soybean oil (ESO) is one such renewable material that has been investigated as a plasticizer for PLA [26, 27].

### **2.3 Soybean oils**

Vegetable oils have become more attractive recently since they are obtained from renewable resources and also have other environmental benefits. They are triglyceride molecules to which three fatty acid groups or esters are attached (Figure 2.3). The long fatty acid chains of vegetable oils impart desirable flexibility and toughness to some brittle resin systems such as epoxy, urethane and polyester resins [28]. The different types of triglyceride vegetable oil include soybean, sunflower, castor, linseed, peanut, etc.

Soybean oil is one of the major vegetable oils that is being cultivated and used in hundreds of products. Having a wide range of uses from food to inks and paints to plastics, soybeans are an important ingredient in many industrial productions [29]. Out of the 8.3 million tons of soybean oil consumed in USA, only 3% is used for industrial applications. Functionalized soybean oil is available for various applications in coatings and plasticizer additives [30].

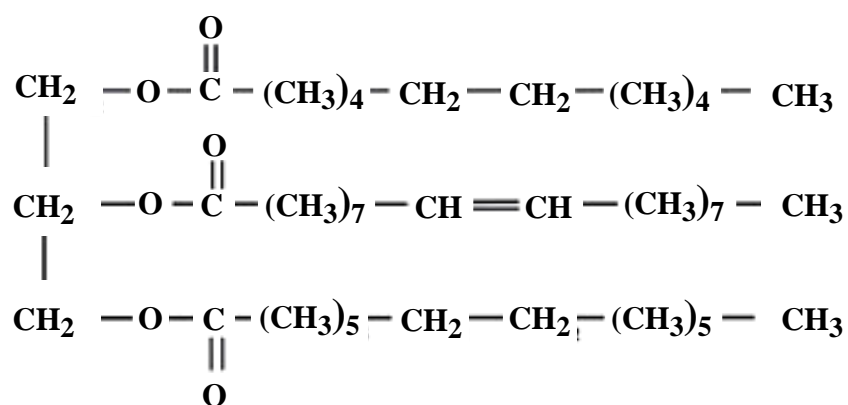


Figure 2.3: Schematic representation of triglyceride structure in vegetable oils [31]

### 2.3.1 Synthesis of ESO

The conventional method of preparing epoxidized vegetable oils involves a reaction where the carbon double bonds of unsaturated fatty acids are epoxidized via catalysis, producing epoxy functional groups (Figure 2.4). Vegetable oils with a high content of unsaturated fatty acid produce materials with high epoxy functionality [32]. Most fatty acids in soybean oil are unsaturated, constituted of about 94.4% of triglycerols, thereby enabling it to have high epoxy functionality materials. The major



fatty acid in soybean oil is linoleic acid, followed by oleic, palmitic, linolenic, and steric acids [28, 29].

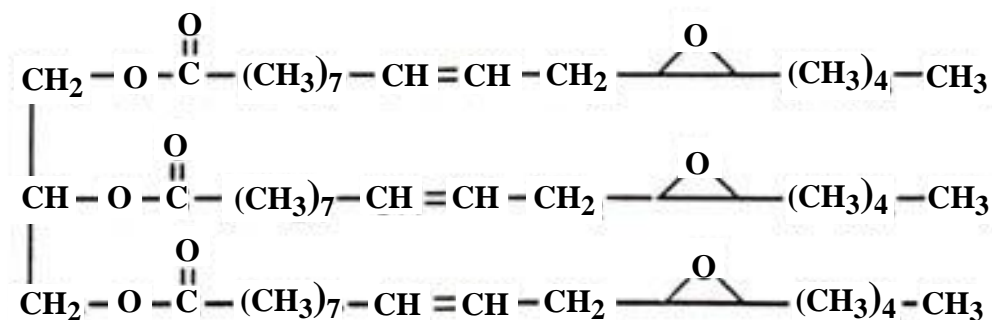


Figure 2.4: Structure of Epoxidised Soy Oil (ESO)<sup>[33]</sup>

There are four known technologies to produce epoxides from olefinic molecules:

- (a) epoxidation with percarboxylic acids, the most widely used in the industry, which can be catalyzed by acids or by enzymes;
- (b) epoxidation with organic and inorganic peroxides which includes alkaline and nitrile hydrogen peroxide epoxidation as well as transition metal catalyzed epoxidation;
- (c) epoxidation with halohydrins, using hypohalous acids (HOX) and their salts as the reagents for the epoxidation of olefins with electron deficient double bonds;
- and (d) epoxidation with molecular oxygen [28].

### ***2.3.2 Use of ESO as a plasticizer***

ESO is used as a non-toxic plasticizer for non-degradable polymers such as PVC compounds, phenolic resins, and chlorinated rubbers to improve stability and flexibility [34]. The work by Ishiaku and coworkers indicated that ESO is an ideal plasticizer for the PVC/ENR (epoxidized natural rubber) system, with the blend exhibiting good tear strength, good tensile strength, and a lower glass transition temperature [35]. Other investigators observed that ESO increases the flexibility of phenolic resins and improves the electrical properties, solvent resistance, and heat resistance of laminates [36]. Recently, ESO has been reported to be an effective plasticizer for biodegradable polymers because of its excellent plasticizer performance and great efficiency of plasticization [37].

ESO has been used as a plasticizer for PLA to improve its properties. Studies have been conducted on the rheological and tensile properties of PLA/ESO blends [26, 27]. Investigations have shown that the addition of ESO into PLA lowers the  $T_g$ , storage modulus and viscosity of the blend while improving the elongation at break [26]. Other studies reported increased elongation at break and melt strength in PLA/ESO blends compared to neat PLA [27]. Additionally, the melt strength was correlated with the ESO content and higher melt strength was obtained by adding higher ESO content in the blend, which resulted in higher elongation at break for the blend [27].

Although ESO has been reported to be an effective plasticizer for bio-degradable polymers due to its excellent permanency and efficiency of plasticization [37], research conducted so far on PLA plasticized with ESO has mostly focused on the effects of plasticizer types and/or addition levels on the mechanical properties without due

consideration of the processing methods for these blends. Several multi-step approaches of formulating PLA/ESO blends have been investigated [23, 25]. In most studies ESO is pre-mixed with PLA prior to shaping the blends in an extruder or using other processing techniques [27]. This study will explore the feasibility of a novel one-step continuous process of blending of ESO and PLA needed for the manufacture of flexible PLA sheet and film.

## **2.4 Processing technologies for PLA**

The main conversion methods for PLA involve melt processing, where PLA is melted and then formed into desired shapes and dimensions before cooling to stabilize the parts. These methods include conventional processing technologies such as extrusion, injection molding, injection stretch blow molding, casting, blown film, thermoforming, etc. Since all of these methods are based on melt processing, it is essential to understand the thermal, crystallization, and melt rheological properties of PLA to optimize the processes [38].

### ***2.4.1 Drying and extrusion***

Prior to melt processing, PLA is required to be dried sufficiently to prevent excessive hydrolysis which affects the physical properties of the polymer [38]. Typically, the polymer is dried to less than 100 ppm moisture content before extrusion. Extrusion is the most important technique for continuous melt processing of PLA. An extruder is usually a part of forming machine systems for injection molding, blow molding, film blowing and melt spinning [38].

### ***2.4.2 Injection molding***

Injection molding is the most widely used converting process for thermoplastic articles requiring complex shape with high dimensional precision. Most injection molding machines for PLA are based on the reciprocating screw extruder, although two-stage systems, which integrate a shooting pot and extruder in a single machine, are also being used for injection molding of preforms for PLA bottles. The two-stage system consists of an in-line extruder integrated to a shooting pot. In the two-stage systems, the extruder plasticizes and feeds the melt into the shooting pot under relatively low injection pressure, from which the melt is injected into the hot runner under high pressure by a plunger in the shooting pot. While the reciprocating machine must stop the screw during the injection and packing phases, the screw for the two-stage machine can rotate during the majority of the cycle. The two-stage system presents some advantages over its reciprocating counterpart, including shorter cycle time, small screw motor drive, more consistent melt quality, and more consistent shot size [39]. In general, injection molded PLA articles are relatively brittle due to rapid physical aging. Process parameters such as mold temperature, packing pressure, cooling rate, and post-mold cooling treatment are expected to influence the PLA aging behavior [38].

### ***2.4.3 Stretch blow molding***

The food industry has shown sustained interest in the use of PLA bottles for beverages that are not sensitive to oxygen such as water or pasteurized milk. These PLA bottles are generally produced by the injection stretch blow molding technique which involves biaxial orientation of PLA to improve physical and barrier properties. The

molecular orientation induced in this process also reduces effects of aging by stabilizing the polymer free volume [40]. This technique involves the formation of a parison, which is then transferred to a blow molding machine where it is stretched in the axial direction and blown in the hoop direction to achieve biaxial orientation [38].

#### ***2.4.4 Thermoforming***

Thermoforming is commonly used in making packaging containers that do not require complicated features. PLA has been thermoformed into disposable cups, food trays, and blister packaging. The technique involves heating the PLA sheet to soften the polymer and forcing it either pneumatically or mechanically against the mold, following by cooling and removing from the mold. In the thermoformed PLA containers, the regions that are highly drawn are less brittle indicating that orientation increases toughness in PLA. Typically aluminum molds are used when thermoforming PLA containers [38].

#### ***2.4.5 Cast film and sheet***

Typically films ( $\leq 0.076$  mm or 0.003 in thick) and sheets ( $\geq 0.254$  mm or 0.01 in thick) are produced in a similar method by the cast film extrusion technique. Sheet and film forming is achieved on a three-roll horizontal stack where the molten PLA is extruded through a die and quenched on polished chrome rollers that are cooled with circulating water. The rate of extrusion, draw rate, temperature and ratio determine the thickness of the sheet or film produced. PLA can be co-extruded with other polymers to form multi-layer structures using this technique, to enhance its properties [38].

#### ***2.4.6 Extrusion blown film***

In extrusion blown film technique, PLA is extruded through an annular die to form a tube that is inflated into a bubble by blowing air through the die head. The bubble is then cooled and flattened at the nip rollers and collected by the winder. Films of different thickness and different degree of orientation can be obtained by varying the blow-up-ratio (ratio of bubble diameter to the die diameter), screw speed, air pressure, and winder speed. The weak melt strength of PLA makes it difficult to form a stable bubble and hence requires the use of additives such as viscosity enhancers to increase its melt strength. Also, since PLA is brittle, stiff and has low elongation, flattening of the bubble at the nip rollers tends to produce wrinkles that are permanent, due to the high dead-fold properties of PLA. This can be overcome by the use of fillers which can reduce the adhesion between films [38].

Thellen and coworkers produced plasticized blown film with an average thickness of 0.076 mm and studied the effects of process parameters such as screw speed and feed rate on the properties of montmorillonite layered silicate (MLS)/ PLA films. The biaxial orientation of the blown film produced improved the dispersion of the MLS platelets in the PLA polymer matrix [41]. Other investigators produced blown films (45  $\mu\text{m}$  thick) from a mono extrusion blown molding machine to test the biodegradation of PLA under natural conditions [42]. However, we found no reports of PLA/ESO blown films. This study will explore the feasibility of a novel one-step continuous method of blending of ESO and PLA needed for the extrusion of flexible PLA blown films.

## REFERENCES

## 2.5. References

1. Hartmann, M.H. and Kaplan D. L., *Biopolymers from Renewable Resources*, Springer – Verlag, Berlin, pp. 367-411 (1998).
2. Lee, S.Y., Kang, I.A., Doh, G.H., Yoon, H.G., Park, B.D., and Wu, Q., Thermal and mechanical properties of wood flour/talc-filled polylactic acid composites: Effect of filler content and coupling treatment, *Journal of Thermoplastic Composite Materials*, 21 (3): 209-23 (2008).
3. Pilla, S., Gong, S., O'Neill, E., Rowell, R.M., and Krzysik, A.M., Polylactide-pine wood flour composites, *Polymer Engineering and Science*, 48: 578-87 (2008).
4. Oksman, K., Skrifvars, M., and Selin, J.F., Natural fibers as reinforcement in polylactic acid (PLA) composites, *Composites Science and Technology*, 63: 1317-24 (2003).
5. Auras, R., Harte, H., and Selke, S., An overview of polylactides as packaging materials, *Macromolecular Biosciences*, 4: 835-864 (2004).
6. Garlotta, D., A literature review of poly(lactic acid), *Journal of Polymers and the Environment*, 9 (2): 63-84 (2001).
7. Wu, J., Hu, Y., Zhou, J., Qian, W., Lin, X., Chen, Y., Chen, X., Xie, J., and Ying, H., Separation of D-lactic acid from aqueous solutions based on the adsorption technology, *Colloids and Surfaces A: Physiochemical and Engineering Aspects*, 407: 29-37 (2012).
8. Pacetti, S.D., Hossainy, S.F.A., and Gale, D.C., Amorphous poly(D,L-Lactide) coating, Patents, Patent number EP1879971 A1, Europe
9. Jiang, X., Luo, Y., Tian, X., Huang, D., Reddy, N., and Yang, Y., Poly(lactic acid) synthesis, structures, properties, processing, and applications, John Wiley & Sons, Inc.: Hoboken, N.J. pp 69-82 (2010).
10. Smith, R., Biodegradable polymers for industrial applications, Woodhead; CRC Press, Cambridge, Boca Raton, FL, pp 37-42 (2005).
11. Urayama, H., Moon, S. I., and Kimura, Y., Microstructure and thermal properties of polylactides with different L- and D-unit sequences: Importance of the helical nature of the L-sequenced segments, *Macromolecular Materials and Engineering*, 288: 137-143 (2003).
12. Colomines, G., Ducruet, V., Courgneau, C., Guinault, A., and Domenech, S., Barrier properties of poly(lactic acid) and its morphological changes induced by aroma compound sorption, *Polymer International*, 59: 818-826 (2010).



13. Cygan, Z., Improving processing and properties of polylactic acid, *Plastic Trends*, 20: 49 (2009).
14. Auras, R., Lim, L.T., Selke, S., and Tsuji, H., Poly(lactic acid) – Synthesis, structures, properties, processing and applications, John Wiley & Sons, Inc., New Jersey (2010).
15. Lehermeier, H.J., Dorgan, J.R., and Way, D., Gas permeation properties of poly(lactic acid), *Journal of Membrane Science*, 190: 243-251 (2001).
16. Liu, H., and Zhang, J., Research progress in toughening modification of poly(lactic acid), *Polymer Physics*, 49: 1051-1083 (2011).
17. Nampoothiri, K.M., Nair, N.R., and John, R.P., An overview of the recent developments in polylactide (PLA) research, *Bioresource Technology*, 101: 8493-8501 (2010).
18. Jacobsen, S. and Fritz, H.G., Plasticizing polylactide - The effect of different plasticizers on the mechanical properties, *Polymer Engineering and Science*, 39: 1303-1310 (1999).
19. Ishida, S., Nagasaki, R., Chino, K., Dong, T., and Inoue, Y., Toughening of poly (L-lactide) by melt blending with rubbers, *Journal of Applied Polymer Science*, 113 (1): 558-66 (2009).
20. Afrifah, K.A. and Matuana, L.M., Impact modification of polylactide with a biodegradable ethylene/acrylate copolymer, *Macromolecular Materials and Engineering*, 295: 802-811 (2010).
21. Matuana, L.M., Solid state microcellular foamed poly(lactic acid): Morphology and property characterization, *Bioresource Technology*, 99: 3643-3650 (2008).
22. Ljungberg, N. and Wesslen, B., The effects of plasticizers on the dynamic mechanical and thermal properties of poly(lactic acid), *Journal of Applied Polymer Science*, 86: 1227-1234 (2002).
23. Baiardo, M., Frisoni, G., Scandola, M., Rimelen, M., Lips, D., Ruffieux, K. and Wintermantel, E., Thermal and mechanical properties of plasticized poly(L-lactic acid), *Journal of Applied Polymer Science*, 90: 1731-1738 (2003).
24. Martino, V.P., Jimenez, A., and Ruseckaite, R.A., Processing and characterization of poly(lactic acid) films plasticized with commercial adipates, *Journal of Applied Polymer Science*, 112: 2010-2018 (2009).
25. Robertson, M.L., Chang, K., Gramlich, W.M., and Hillmyer, M.A., Toughening of polylactide with polymerized soybean oil, *Macromolecules*, 43: 1807-1814 (2010).

26. Ali, F., Chang, Y.W., Kang, S.C., and Yoon, J.Y., Thermal, mechanical and rheological properties of poly(lactic acid)/epoxidized soybean oil blends, *Polymer Bulletin*, 62: 91-98 (2009).
27. Xu, Y.Q. and Qu, J.P., Mechanical and rheological properties of epoxidized soybean oil plasticized poly(lactic acid), *Journal of Applied Polymer Science*, 112: 3185-3191 (2009).
28. Saremi, K., Tabarsa, T., Shakeri, A., and Babanalbandi, A., Epoxidation of soybean oil, *Annals of Biological Research*, 3 (9): 4254-4258 (2012).
29. Hammond, E.G., Johnson, L.A., Su, C., Wang, T., and White, P.J., Bailey's Industrial Oil and Fat Products, John Wiley & Sons, Inc, pp 577-653 (2005).
30. Miyagawa, H., Mohanty, A.K., Burgueño, R., Drzal, L.T., and Misra, M., Novel biobased resins from the blends of functionalized soybean oil and unsaturated polyester resin, *Journal of polymer Science*, 45: 698-704 (2007).
31. Song, B., Chen, W., Liu, Z., and Erhan, S.Z., Compressive mechanical behavior of soybean oil-based polymers at low and high strain rates, *Journal of Applied Polymer Science*, 99: 2759-2770 (2006).
32. Meyer, P., Techaphattana, N., Manundawee, S., Sangkeaw, S., Junlakan, W., and Tongurai, C., Epoxidation of soybean oil and jatropha oil, *Thammasat International Journal of Science and Technology*, 13: 1-5 (2008).
33. Mannejote, J.K. AND Kailas, S.V., The effect of oxidation on the tribological performance of few vegetable oils, *Journal of Materials Research and Technology*, 1(2): 91-95 (2012).
34. Zhu, J., Chandrashekhara, K., Flanigan, V., and Kapila, S., Manufacturing and mechanical properties of soy-based composites using pultrusion, *Composites Part A: Applied Science and Manufacturing*, 35 (1): 95-101 (2004).
35. Ishiaku, U.S., Shaharum, A., Ismail, H., and Mohd Ishak, Z.A., The effect of an epoxidized plasticizer on the thermo-oxidative ageing of poly(vinyl chloride)/epoxidized natural rubber thermoplastic elastomers, *Polymer International*, 45: 83-91 (1998).
36. Konii, S., Yoshimura, Y., Nanaumi, K., Yasuzawa, K., Yoshida, T., and Shinko, T., Process for producing internally plasticized phenolic resins, US patent P4209429 (1980).

37. Zhao, Y., Qu, J., Feng, Y., Wu, Z., Chen, F., and Tang, H., Mechanical and thermal properties of ESO plasticized polybutyl succinate blends, *Polymers for Advanced Technologies*, 23: 632-638 (2012).
38. Lim, L.T., Auras, R., and Rubino, M., Processing technologies for poly(lactic acid), *Progress in Polymer Science*, 33 (8): 820–852 (2008).
39. Rees H., Understanding injection molding technology, Cincinnati: Hanser/Gardner Publications, Inc.; (1995).
40. Witzke D.R., Introduction to properties, engineering, and prospects of polylactide polymers. PhD Thesis. Michigan State University, East Lansing, MI, USA (1997).
41. Thellen, C., Orroth, C., Froio, D., Ziegler, D., Lucciarini, J., Farrell, R., D'Souza, N.A., and Ratto, J.A., Influence of montmorillonite layered silicate on plasticized poly(l-lactide) blown films, *Polymer*, 46: 11716-11727 (2005).
42. Sedlarik, V., Saha, N., Sedlarikova, J., and Saha, P., Biodegradation of blown films based on poly(lactic acid) under natural conditions, *Macromolecular Symposia*, 272: 100-103 (2008).

## Chapter 3

### EXPERIMENTAL

#### 3.1 Materials

Semi-crystalline PLA (2002D grade) from NatureWorks (USA) was used as the resin in this study. Its properties are listed in Table 3.1. Galata Chemicals supplied the epoxidized soybean oil, commercially known as Drapex<sup>®</sup> 6.8, which was used as a plasticizer. It had a density of 0.992 g/cm<sup>3</sup>, flash point of 290°C, oxirane content of 7%, iodine value of 1.6, and was insoluble in water.

Table 3.1. Characteristics of PLA (2002D) resin used in this study<sup>[1]</sup>.

| Density of<br>solid (g/cm <sup>3</sup> ) | Melt properties <sup>a</sup> |                                   | Thermal properties <sup>b</sup> |       |
|--|------------------------------|-----------------------------------|---------------------------------|-------|
|  | MFR                          | $\rho_m$                          | $\chi_c$                        | $T_m$ |
|  | (g/10 min)                   | (g/cm <sup>3</sup> ) <sup>2</sup> | (%)                             | (°C)  |
| 1.256                                    | 3.4                          | 1.142                             | 15                              | 149   |

<sup>a</sup>MFR and  $\rho_m$  are the melt flow rate and melt density of PLA, respectively.

<sup>b</sup> $T_m$  and  $\chi_c$  are the melting temperature and percent crystallinity of PLA, respectively.

### 3.2 Sample manufacturing

Both sheets and films were evaluated. The methods employed to manufacture these samples were as follows:

#### *3.2.1 Manufacture of plasticized sheets*

Several multi-step approaches to formulating PLA/ESO blends have been investigated [2, 6]. The goal of this study was to develop a one step approach of blending PLA with ESO during sheet manufacturing. To achieve this goal, it was crucial to develop a continuous and accurate system for incorporating ESO into the matrix during processing. This was attained by attaching an extruder and an injection pump in a tandem way so that accurate amounts of plasticizer could be injected into the molten PLA in the barrel of the extruder.

A co-rotating segmented twin screw extruder (TSE DSE 25) (C.W. Brabender Instruments Inc.) with a screw diameter of 25 mm and a length-to-diameter ratio of 32:1 was used to melt and shape the blends into sheets. Its segmented screws were composed of conveying, shearing, and mixing elements. The extruder was fitted with a rectangular profile die with dimensions of 50.8 mm (width) by 3 mm (thickness) and was powered by a 5.6 kilowatt (7.5 hp) Intelli-Torque Plasti-Corder Torque Rheometer® (C.W. Brabender Instruments Inc.). Additionally, a single screw dosing unit (Color-Exact Type 1000 Plastic Recycling Machinery Aps) was connected to the extruder. A digital variable speed peristaltic injector pump (Omega Inc.), which is an externally controllable pump, was used to accurately meter various amounts of plasticizer into the PLA blends. The

schematic of the tandem extrusion-injection pump system used in this study is shown in Figure 3.1.

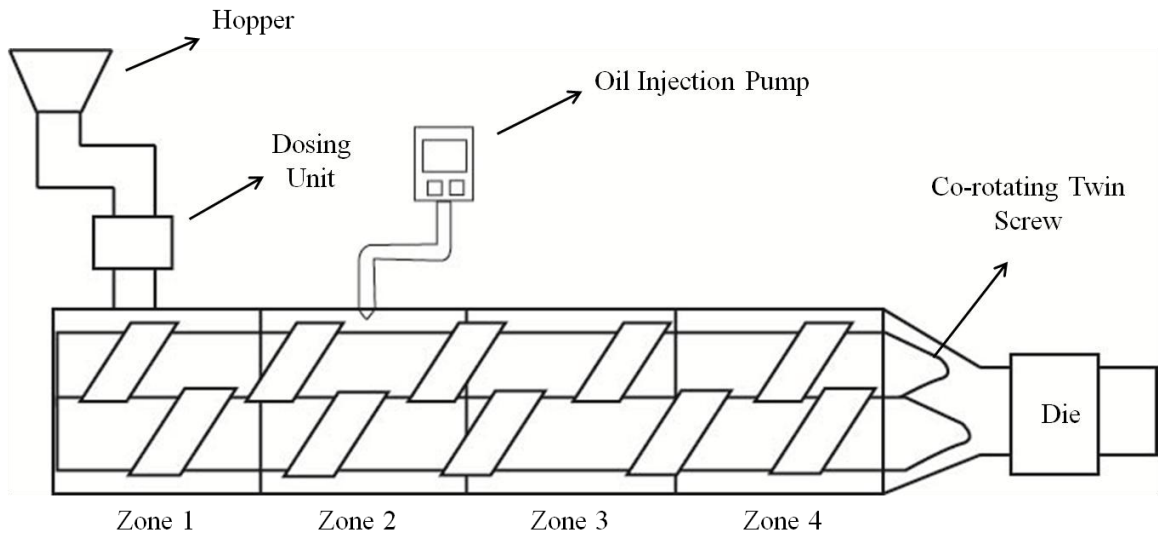


Figure 3.1: The schematic representation of the tandem extrusion-injection pump system used in this study.

Prior to blending PLA with plasticizer, it was important to individually calibrate the dosing unit attached to the extruder and the injector pump as well as in order to derive regression equations needed in the calculations of the desirable nominal amounts of PLA and plasticizer in the blends.

Since the flow rate (extruded output) of melted plastic is independent of the rotational screw speed in a segmented twin screw extruder, the calibration of the amount of PLA needed in the blends was carried out by changing the screw speed of the dosing unit instead, which resulted in various melt flow rates for PLA. From the hopper of the dosing unit, a feed screw conveyed PLA pellets at different speeds to a dome through

which they fell freely into the feeding barrel of the extruder with screws running at a constant rotational speed of 100 rpm throughout the experiments. Starting from the hopper to the die, the melt blending temperature profile was set at 180-175-175-170-165°C. The dosed quantities of melted PLA were then collected over a period of time, and weighed for flow rate measurements from which a calibration curve was plotted and the regression equation derived (Figure 3.2).

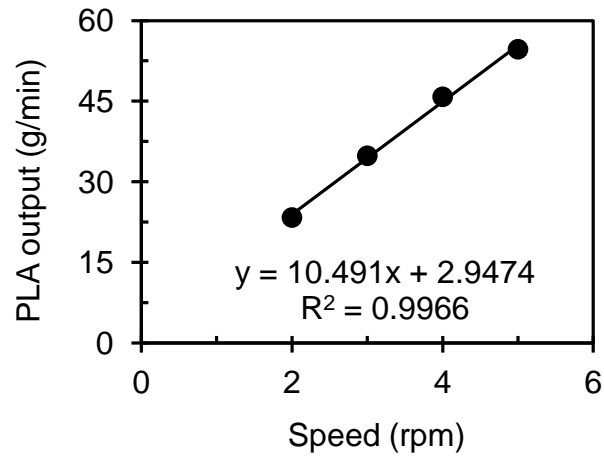


Figure 3.2: Calibration curve for determining the nominal amount of extruded PLA in the blends.

The calibration of the nominal amount of plasticizer (ESO) injected into the molten PLA during processing was performed similarly. Various amounts of ESO were injected in an empty beaker by changing the percent injection speed of the pump. Dosed quantities of ESO were collected over a period of time and weighed to determine the output, from which the calibration curve was plotted and the regression equation derived (Figure 3.3).

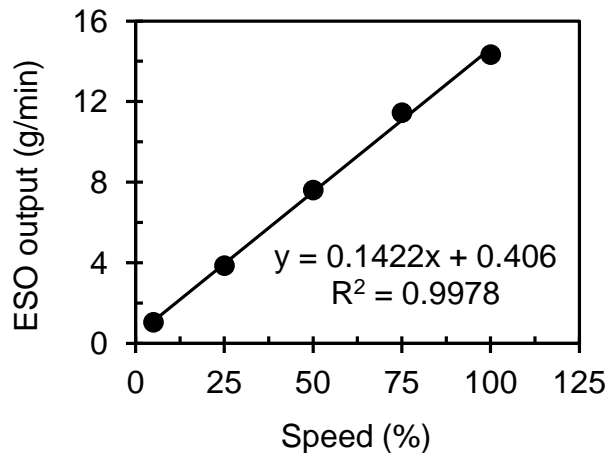


Figure 3.3: Calibration curve for determining the nominal amount of ESO injected in the blends.

The regression equations and/or calibration curves shown in Figures 3.2 and 3.3 were utilized to determine the amounts of injected ESO and dosed PLA so that the blends contained accurate concentrations of each component. For example, to extrude 50 g of PLA/ESO blend made of 80% PLA (40 g of PLA) and 20% ESO (10 g of ESO), one should set the dosing unit's screw speed and the pump injection percent speed at approximately 3.53 rpm and 67.5%, respectively. This approach was followed throughout the experiments to produce sheets containing various ESO contents (0 to 20 wt %). It should be mentioned that PLA was dried in an oven at 55°C for at least 24 hours prior to processing to remove residual moisture.



### ***3.2.2 Manufacture of plasticized films***

Films were produced for only unplasticized PLA (neat PLA) and PLA plasticized with 15 wt % ESO. The blend of PLA plasticized with 15 wt % ESO was melt mixed using the system and processing conditions described above. The melt blended materials were cooled for about an hour at room temperature and granulated in a Conair Wortex granulator (Model JC-5). Granulated samples were then dried in an oven at 55°C for about 24 hours and blown into films using a 19 mm single-screw extruder (C.W. Brabender Instruments Inc.) with a length-to-diameter ratio of 15:1. This extruder was powered by a 3.73 kilowatt (5 hp) Prep Center<sup>®</sup> D52 (C.W. Brabender Instruments Inc.) and fitted with a blown film die 25.4 mm in diameter with 0.889 mm (0.035") extrudate wall thickness. Starting from the hopper to the die, the temperature profile of the extruder was set at 180-175-170-165°C.

Processing parameters such as the blow up ratio (BUR), the extruder's rotational screw speed, the speed of the pull up nip rollers or draw ratio (DR), and the air pressure inside the inflated plastic have strong effects on the thickness of the films. All these variables were kept constant throughout the experiments. Specifically, the speeds of the extruder's rotational screw and the pull up rolls for film take off were set at 30 rpm and 25 rpm, respectively, while the air pressure used to inflate the film varied slightly between 0.310 and 0.379 MPa (45 and 55 psi) during the extrusion process. The blow up ratio and draw ratio of blown films (~0.076 mm thick) were calculated using the following equations and were found to be approximately 3 and 11.7, respectively.

$$\text{BUR} = \frac{R_f}{R_o} \quad (3.1)$$

$$\text{DR} = \frac{T_o}{T_f} \quad (3.2)$$

where  $R_f$  and  $R_o$  are the radius of the annular die and the radius of the final tubular film, respectively, and  $T_o$  and  $T_f$  are the thicknesses of the undrawn (0.889 mm) and extrusion blown films, respectively.

### 3.3 Property evaluation

#### 3.3.1 Mechanical properties

The mechanical properties of both sheets and films were characterized, including the tensile strength, tensile modulus, elongation at yield, elongation at break, notched Izod impact strength, burst pressure, and sealing strength. These tests were carried out in a walk-in conditioning room at  $23^\circ\text{C} \pm 2^\circ\text{C}$  and  $50\% \pm 4\%$  relative humidity.

Tensile properties of the sheets ( $\sim 2.75$  mm thick) were measured with an Instron 5585H testing machine using the Instron Bluehill 2, version 2.14 software, in accordance with the procedures outlined in ASTM standard D 638. Each formulation included ten tested replicates to obtain a reliable mean and standard deviation, using a crosshead speed of 5 mm/min. From the tensile results, the ductility, or the material's ability to undergo plastic deformation without fracture, was determined using the following relation:

$$Ductility = \frac{Failure\ strain}{Yielding\ strain} \quad (3.3)$$

Notched Izod impact tests of sheets were performed at room temperature in conformance to ASTM standard D 256 on a Tinius Olsen Izod impact tester (Model 892). The ten specimens tested for each composition were V-notched at a 45<sup>o</sup> angle using a Tinius Olsen specimen notcher (Model 899).

Tensile and Izod impact properties were used to assess the effect of plasticizer concentration on the mechanical properties of the extruded sheets. The results of this part of the study led to the identification of the amount of ESO that caused the brittle to ductile transition in PLA samples as well as the optimum amount of ESO that produced maximum ductility.

As a result, tensile properties of blown films were characterized for unplasticized PLA (control) but only one plasticized PLA formulation containing 15 wt % ESO (optimized amount from previous tests as will be discussed later). Unlike for the sheet samples, tensile properties of plasticized films were measured as a function of time over a span of 125 days to understand the aging of films stored over a long period of time under normal environmental conditions. Tensile properties of the film (~ 0.076 mm thick) were measured with an Instron 5565H testing machine using the Instron Bluehill 2, version 2.21 software and in accordance with the procedures outlined in ASTM standard D882. Ten replicates were tested to obtain a reliable mean and standard deviation using a crosshead speed of 12.5 mm/min. From tensile results, the ductility was determined using equation 3.3.

The sealing strengths of neat PLA film and its counterpart plasticized with 15 wt % ESO were also measured as a function of sealing temperatures. An Impulse sealer Vertrod (Model 14EP-WC) with sealing voltage in the range of 115-120 AC was used to seal the samples using three different sets of high point and low point temperatures of 100-120<sup>o</sup>C, 100-135<sup>o</sup>C, and 100-150<sup>o</sup>C. The strength of the seals was tested in accordance with the procedures outlined in ASTM standard F88. Ten replicates of each of the sealing conditions were tested to obtain a reliable mean and standard deviation.

Similarly, the burst pressures of pouches made with neat PLA film and its counterpart plasticized with 15 wt % ESO were measured as a function of sealing temperature using the Test-A-Pack 2000. The samples were cut into a 10 cm ×10 cm pouches and sealed (3 side-sealed) using the impulse sealer at the three different sealing temperatures mentioned above. The equipment was set to an air supply of 0.621 MPa (90 psi) and prefilled before burst testing. Three replicates of samples sealed at each of the different sealing temperatures were tested.

### ***3.3.2 Thermal properties***

The glass transition temperatures ( $T_g$ ) of PLA plasticized with various amounts of ESO were determined using a Q200 Differential Scanning Calorimeter (TA instruments). Samples weighing less than 10 mg were tested in the temperature range of 40°C to 200°C at a heating rate of 10<sup>o</sup>C/min. A dynamic mechanical analyzer (TA instruments) was also used as a complimentary technique to determine the  $T_g$  of the different PLA/ESO blends.

Samples were subjected to a dual cantilever at a frequency of 1 Hz and were heated over a temperature range of 25 °C to 140 °C at the rate of 5 °C/min.

### ***3.3.3 Phase morphology evaluation***

The miscibility and the phase morphology of the blends were examined by scanning electron microscopy (SEM) analysis. A Carl Zeiss EVO LS 2 with an acceleration voltage of 15kV was used to obtain the micrographic images of the different blends of PLA/ESO. Micrographic images of neat PLA and blends with 10 wt % ESO were taken at 20 µm scale, while blends with 20 wt % ESO was taken at a 30 µm scale to better understand the phase morphology at such high concentration of ESO. SEM micrographs were taken after coating the surfaces with a thin layer of gold.

### ***3.3.4. Statistical analysis***

Unless otherwise mentioned, a one-way analysis of variance (ANOVA) was performed on all mechanical properties of the sheets and the data were analyzed to distinguish statistical differences ( $p < 0.05$ ) between unplasticized (control) and PLA sheets plasticized with various amounts of ESO. Similarly, a one-way ANOVA was used for the statistical analysis of the effect of storage time on the ductility of plasticized films. However, for the burst pressure and seal strength, a two-sample *t*-test and Duncan's multiple range tests were employed to determine the statistical differences among the variables investigated, at a 95% significance level. Comparisons were done between neat and plasticized samples under different sealing temperatures. All statistical analyses were performed using Design Expert software (v. 7) from Stat-Ease (Minneapolis, MN).

## REFERENCES

### 3.4 References

1. Matuana, L.M., Faruk, O., and Diaz, C.A., Cell morphology of extrusion foamed poly(lactic acid) using endothermic chemical foaming agent, *Bioresources Technology*, 100 (23): 5947-5954 (2009).
2. Baiardo, M., Frisoni, G., Scandola, M., Rimelen, M., Lips, D., Ruffieux, K. and Wintermantel, E., Thermal and mechanical properties of plasticized poly(L-lactic acid), *Journal of Applied Polymer Science*. 90: 1731-1738 (2003).
3. Ljungberg, N. and Wesslen, B., Preparation and properties of plasticized poly(lactic acid) films, *Biomacromolecules*, 6: 1789-1796 (2005).
4. Semba, T., Kitagawa, K., Ishiaku, U.S., and Hamada, H., The effect of crosslinking on the mechanical properties of polylactic acid/polycaprolactone blends, *Journal of Applied Polymer Science*, 101, 1816-1825 (2006).
5. Siracusa, V., Blanco, I., Romani, S., Tylewicz, U., Rocculi, P., and Rosa, M.D., Poly(lactic acid)-modified films for food packaging application: physical, mechanical, and barrier behavior, *Journal of Applied Polymer Science*, 125: E390-E401(2012).
6. Robertson, M.L., Chang, K., Gramlich, W.M., and Hillmyer, M.A., Toughening of polylactide with polymerized soybean oil, *Macromolecules*, 43: 1807-1814 (2010).

## Chapter 4

### RESULTS AND DISCUSSION

#### 4.1 Effect of ESO content on the notched Izod impact strength of PLA sheets

The variation of impact strength with different amounts of ESO in the blends is illustrated in Figure 4.1. The impact strength of the blends remained nearly unchanged up to 5 wt % ESO content and then increased significantly with increasing ESO content. Figure 4.1 clearly shows the brittle-to-ductile transition of the impact strength of PLA with an increase in ESO concentration. The threshold ESO content at which the transition from brittle-to-ductile behavior in PLA blends occurred in the range between 5 and 10 wt % ESO content.

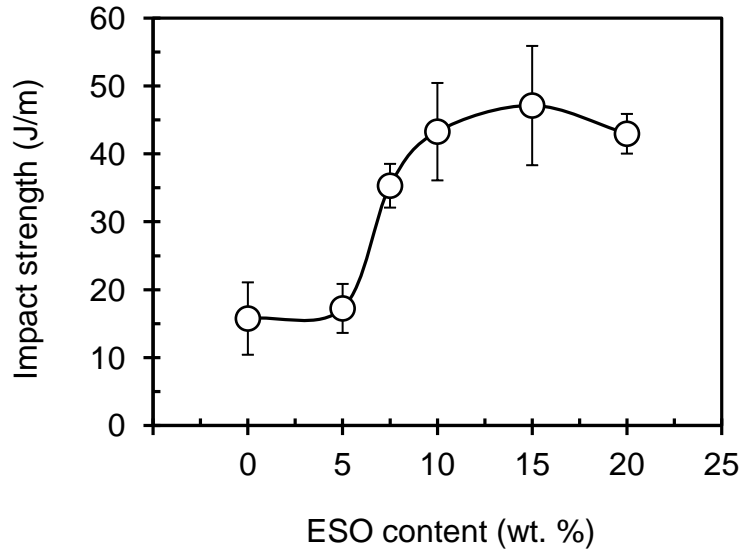


Figure 4.1: Effect of ESO content on the impact strength of PLA.



It was essential to understand the morphology of the ESO and its miscibility with PLA in order to explain the brittle-to-ductile transition of the PLA/ESO blend. Miscibility plays an important role in toughening of the blend and can be inferred from the solubility parameters of the two components that are blended. The solubility parameters of PLA and ESO are  $20.2 \text{ (MPa)}^{1/2}$  and  $16.8 \text{ (MPa)}^{1/2}$ , respectively [1]. These values show that ESO is partially miscible with PLA since the solubility parameters of PLA and ESO are not the same but are close to each other [1, 2]. Consequently, when ESO is blended with PLA, it may form a second dispersed phase but will not form a complete miscible phase with PLA [2].

The second dispersed phase of ESO has an effect on the crack propagation in the blended polymer. Neat PLA is highly brittle and failure occurs by crazing or micro-cracking where the cracks spread easily and freely. But with the addition of ESO, cracks do not spread freely due to the dispersed second ESO phase. The dispersed second ESO phase can be seen in the SEM images of PLA plasticized with 10 wt % ESO [Figure 4.2 (b)] and 20 wt % ESO [Figure 4.2 (c)] where the plasticizer is seen as droplets dispersed evenly in the PLA matrix. This dispersed ESO phase dissipates a large part of the fracture energy during the crack bifurcation and alters the crack path. This causes increased fracture toughness resulting in increased impact strength [3, 4].

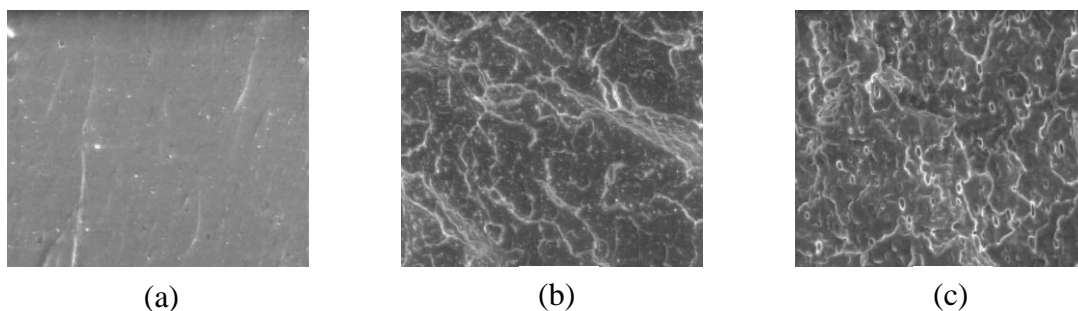


Figure 4.2: SEM micrographs of PLA plasticized with various amounts of ESO: (a) 0 wt %, (b) 10 wt %, and (c) 20 wt %.

The impact strength increased significantly from 5 wt % to 10 wt % ESO and reached a maximum at 10 wt % ESO and started leveling off with any further addition of ESO. Addition of 15 wt % and 20 wt % ESO did not have any statistical significance in the impact strength over 10 wt % ESO. In the blends with 10 wt % ESO or more, PLA and the ESO were assumed to exist in a continuous phase since ESO is partially miscible with PLA. PLA would form the continuous phase owing to its higher concentration in the blend and ESO would form the second dispersed phase that dissipates the fracture energy resulting in improved impact strength.

## 4.2 Effect of ESO content on the tensile properties of PLA sheets

### 4.2.1. *Ductility*

Stress-strain curves showing the effect of ESO content on the tensile properties of plasticized PLA sheets are shown in Figure 4.3. A well-defined yield point before fracture was observed in all stress-strain curves. However, at up to 5 wt % ESO, the stress-strain curves of plasticized sheet overlapped with that of neat PLA [Figure 4.3. (a)], implying an insignificant plasticizing effect when up to 5 wt % ESO was added into PLA matrix. Additionally, the specimens stretched on a relatively narrow range of strain (less than 4%) and no localized neck was formed beyond the yield point, indicative of the brittle nature of the material [5]. These results are in agreement with the impact strength data shown in Figure 4.1, where the incorporation of up to 5 wt % ESO into PLA did not toughen the matrix. By contrast, with 10 wt % or more ESO in PLA, the specimens yielded with stable necking [Figure 4.3. (b)] showing cold-drawing behavior. These blends underwent tensile deformation as indicated by their stress whitening (Figure 4.4), caused by void formation due to crazing of the ductile PLA/ESO blends [6]. This is a morphological indication of the increased toughness in the PLA/ESO blends when compared to that of neat PLA. Additionally, these specimens stretched on a wide range of strain, which is typically observed with toughened plastics.

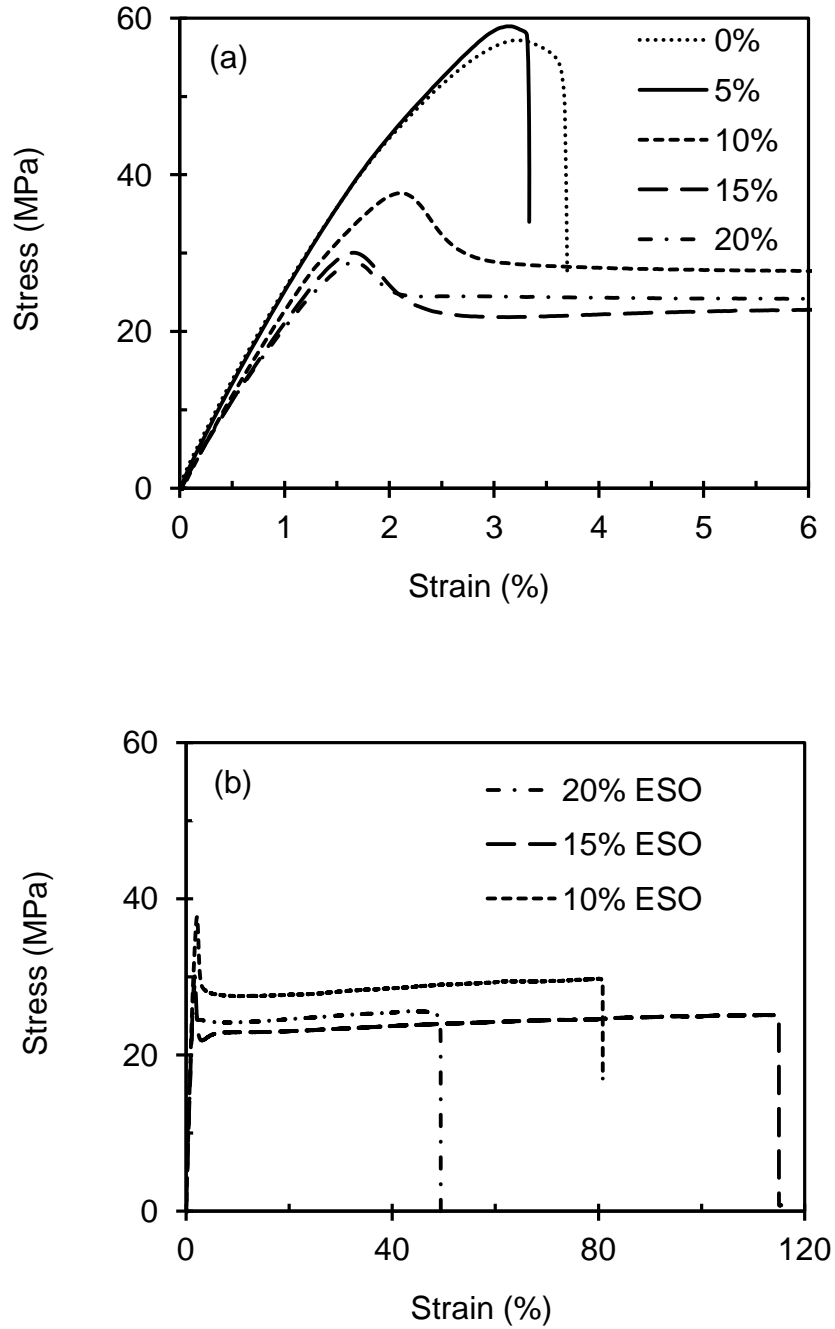


Figure 4.3: Stress-strain curves of (a) unplasticized PLA and PLA plasticized with various amounts of ESO showing well defined yield points and (b) Plasticized PLA showing stable necking beyond yield point.

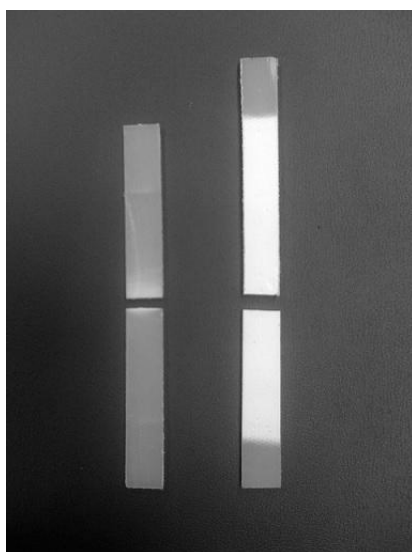


Figure 4.4: Tensile deformation showing the stress whitening in unplasticized PLA (left) and PLA plasticized with 10 wt % ESO (right).

Unplasticized PLA was very brittle, as indicated by its low ductility value (Figure 4.5). The addition of up to 5 wt % ESO into PLA did not affect the ductility of the specimens. Above this concentration, however, a significant increase in ductility occurred by increasing ESO content, confirming the toughening and plasticizing effects of ESO. Notice that the brittle-to-ductile transition also happened in the range between 5 and 10 wt % (Figure 4.5), in agreement with the impact strength results shown in Figure 4.1. This increased flexibility could also be attributed to the partial miscibility between ESO and the PLA matrix where the ESO forms a continuous phase with the PLA, as previously discussed. This morphology results in ductile drawing at the fracture interfaces due to plastic deformation [3].

Like in the case of impact strength, with further increase in the amount of plasticizer, we would expect the ductility values to level off at 10 wt % ESO. However, there was a significant increase in ductility by increasing the ESO content from 10 to 15 wt %. This was followed by a decreased ductility from 49% to 30%, when ESO content was further increased from 15 to 20 wt %. This discrepancy in trend between ductility and impact strength could be due to the systematic errors during experimentation and testing as clearly indicated by the wide error bars (standard errors) of the ductility results shown in Figure 4.5. Nevertheless, the trend showing the brittle-to-ductile transition was still a good indication of the toughening capacity of ESO as a plasticizer for PLA.

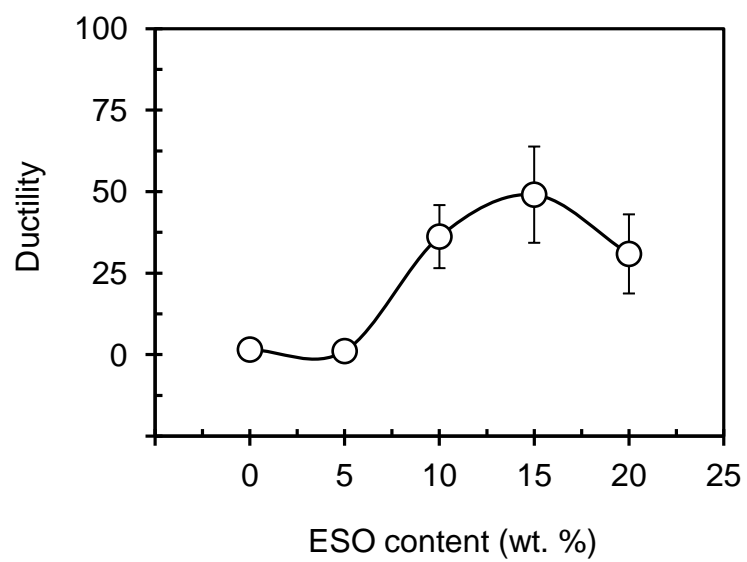


Figure 4.5: Effect of ESO content on the ductility of the PLA sheet.

#### ***4.2.2. Tensile strength and Modulus***

In the case of semi crystalline polymers like PLA, an efficient plasticizer generally reduces the glass transition temperature ( $T_g$ ) of the matrix, thereby increasing its flexibility but at the expense of the tensile strength and modulus, which decrease. Therefore, the  $T_g$  of PLA decreased with the increasing ESO content in the blends as expected (Table 4.1), suggesting increased segmental mobility of the PLA chains due to plasticization. The decreased  $T_g$  was significant when more than 5 wt % ESO was added into PLA matrix.

As expected, this plasticization affected the tensile strength at yield and tensile modulus of the blends (Figure 4.6). Up to 5 wt %, the addition of ESO did not influence the strength or the stiffness of PLA, in agreement with the  $T_g$  results. However, increasing the ESO content above 5 wt % led to a significant decrease in both yield strength and modulus, due to the increased plasticization level of the matrix. As the plasticizer content increased, PLA became softer, more flexible as indicated by the reduced  $T_g$ , more extensible and tougher, resulting in reduced strength and modulus. Similar results were reported for PVC plasticized with dioctyl phthalate [5].



Table 4.1: Effect of ESO content on the glass transition ( $T_g$ ) of PLA (2002D) measured by DSC and DMA.

| ESO content (wt %) | $T_g$ ( $^{\circ}\text{C}$ ) |      |
|--------------------|------------------------------|------|
|                    | DSC                          | DMA  |
| 0                  | 59.5                         | 71.3 |
| 5                  | 58.7                         | 71.9 |
| 10                 | 55.4                         | 69.7 |
| 15                 | 55.0                         | 69.4 |
| 20                 | 53.2                         | 66.0 |

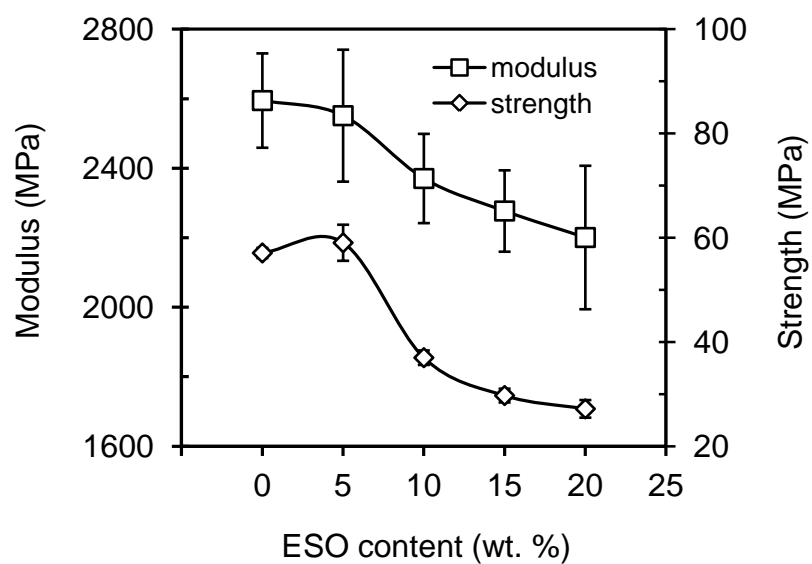


Figure 4.6: Effect of ESO content on the tensile stress at yield and tensile modulus of PLA sheet.

### **4.3. Effect of ESO on package related properties**

Flexible packaging films are used in several applications and can have multiple purposes such as to protect packages during shipment, extend product shelf life, enhance product presentation, etc., which require that a package be designed. This study examined the effect of plasticizer on the heat sealability of PLA film during pouch manufacture by measuring both the burst pressure and seal strength of the pouches.

#### ***4.3.1 Burst pressure of PLA films***

Burst pressure is an indication of the pressure resulting in package failure and is commonly used to evaluate the integrity of retortable pouches. The internal burst test is considered a good overall measure of the ability of the pouch to withstand transport and handling [7].

The burst pressures of pouches made with neat PLA film and its counterpart plasticized with 15 wt % ESO were measured as a function of sealing temperatures (Table 4.2). Adhesive failure did not occur at the interface of the seal, i.e., non peelable seal. Instead, material failure occurred in all pouches, irrespective of the sealing temperature used and the addition of plasticizer in the films. Nevertheless, pouches made of plasticized PLA films failed at a lower burst pressure than their counterparts with unplasticized film (Table 4.2), mainly attributable to the plasticizing, which lowered the strength of plasticized specimens compared to neat PLA films (Figure 4.6). As mentioned, the sealing temperatures investigated did not influence the burst pressure because the package did not experience adhesive failure, i.e., the seals remained intact during burst tests.

#### 4.3.2 Seal strength of PLA films

The integrity of a seal is also a critical step in evaluating the quality of a pouch in packaging. The seal strengths of neat PLA film and its counterpart plasticized with 15 wt % ESO were also measured as a function of sealing temperature using the peel test that measures the maximum force per unit width required to pull apart the seal [7]. The seal strength of PLA was not affected by the addition of plasticizer nor by the sealing temperature studied (Table 4.2).

Table 4.2. Effect of sealing temperature on the burst pressure and sealing strength of unplasticized (neat) PLA and plasticized PLA films.

| Sealing temperature (°C) | Burst pressure (kPa) <sup>1</sup> |                          | Sealing strength (kN/mm) <sup>1</sup> |                          |
|--------------------------|-----------------------------------|--------------------------|---------------------------------------|--------------------------|
|                          | Neat                              | Plasticized <sup>2</sup> | Neat                                  | Plasticized <sup>2</sup> |
| 120-100                  | 66.3 ± 5.3 <sup>A</sup>           | 40.1 ± 1.7 <sup>B</sup>  | 10.1 ± 0.2 <sup>A</sup>               | 9.9 ± 0.2 <sup>A</sup>   |
| 135-100                  | 69.2 ± 1.7 <sup>A</sup>           | 39.1 ± 3.0 <sup>B</sup>  | 9.9 ± 0.1 <sup>A</sup>                | 10.1 ± 0.9 <sup>A</sup>  |
| 150-100                  | 68.2 ± 1.7 <sup>A</sup>           | 41.2 ± 3.6 <sup>B</sup>  | 10.1 ± 0.4 <sup>A</sup>               | 10.3 ± 1.0 <sup>A</sup>  |

<sup>1</sup>The different superscript letters denote that the difference between two treatments is statistically significant (p<0.05).

<sup>2</sup>Plasticized PLA films contained 15 wt % ESO.

#### ***4.3.3 Tensile properties of plasticized films as a function of storage time***

The tensile properties of blown films were characterized for blown PLA films plasticized with 15 wt % ESO (optimized amount). The properties of plasticized films were measured as a function of time over a span of 125 days to understand the aging of the films stored under normal environmental conditions (Table 4.3).

The ductility remained the same with increasing storage time, indicating that the flexibility of plasticized film did not change over the period of time tested. This is an indication of the permanence characteristics of ESO in the PLA/ESO blends. Similar trend was observed for tensile strength; the plasticized PLA films exhibiting the same yield strength values (no statistical significance) after 4 months storage period.

In contrast, the tensile modulus showed a slight but a statistically significant increase in stiffness after only 7 storage days but did not significantly change for the remaining of the testing period (Table 4.3). The modulus of elasticity increased significantly with increasing ESO content to a value closer to that of unplasticized PLA, indicating that the film behaved like unplasticized samples as the storage time increased. The modulus of elasticity of plasticized film increased from 2.29 GPa to 2.55 GPa when tested immediately and 125 days after its manufacture, respectively. These results could indicate a possible loss of plasticizer from the film as the storage time increased. Additional work must be performed to verify this trend, which cannot be explained at the moment.

Table 4.3. Variations in tensile properties of plasticized PLA films as a function of storage time.

| Storage times<br>(days) | Tensile properties <sup>1,2</sup> |                         |                   |
|-------------------------|-----------------------------------|-------------------------|-------------------|
|                         | Ductility                         | Yield Strength<br>(MPa) | Modulus<br>(GPa)  |
| 0                       | $39.7 \pm 14.3^A$                 | $33.6 \pm 2.1^A$        | $2.29 \pm 0.13^A$ |
| 7                       | $42.5 \pm 11.4^A$                 | $34.8 \pm 1.8^A$        | $2.44 \pm 0.13^B$ |
| 45                      | $40.4 \pm 8.7^A$                  | $33.3 \pm 1.8^A$        | $2.51 \pm 0.16^B$ |
| 92                      | $30.3 \pm 15.7^A$                 | $34.1 \pm 2.0^A$        | $2.65 \pm 0.16^B$ |
| 125                     | $29.7 \pm 17.1^A$                 | $32.7 \pm 3.0^A$        | $2.55 \pm 0.23^B$ |

<sup>1</sup>The yield strength and tensile modulus of neat PLA films (unplasticized) were 57.1 MPa and 2.59 GPa, respectively.

<sup>2</sup>The different superscript letters denote that the difference between two treatments is statistically significant ( $p < 0.05$ ).

## REFERENCES

#### 4.4 References

1. Karst, D. and Yang, Y., Using the solubility parameter to explain disperse dye sorption on polylactide, *Journal of Applied Polymer Science*, 96(2): 416-422 (2005).
2. Zhao, Y., Qu, J., Feng, Y., Wu, Z., Chen, F., and Tang, H., Mechanical and thermal properties of epoxidized soybean oil plasticized polybutylene succinate blends, *Polymers Advanced Technology*, 23(3): 632-638 (2012).
3. Zheng, S., Wand, J., and Guo, Q., Miscibility, morphology and fracture of epoxy resin/poly(styrene-co-acrylonitrile) blends, *Polymer*, 37(21): 4667-4673 (1996).
4. Afrifah, K.A. and Matuana, L.M., Impact modification of polylactide with a biodegradable ethylene/acrylate copolymer, *Macromolecular Materials and Engineering*, 295: 802-811 (2010).
5. Matuana, L.M., Park, C.B., and Balatinecz, J.J., The effect of low levels of plasticizer on the rheological mechanical properties of polyvinyl chloride/newsprint-fiber composite, *Journal of Vinyl and Additive Technology*, 3(4): 265-273 (1997).
6. Ali, F., Chang, Y.W., Kang, S.C., and Yoon, J.Y., Thermal, mechanical and rheological properties of poly(lactic acid)/epoxidized soybean oil blends, *Polymer Bulletin* 62: 91-98 (2009).
7. Yam, K.L., Rossen, J., and Wu, X.F., Relationship between seal strength and burst pressure for pouches, *Packaging Technology and Science*, 6: 239-244 (1993).

## Chapter 5

### CONCLUSIONS

#### 5.1 Conclusions

This study was aimed at developing a single-step process that efficiently incorporates ESO into a PLA matrix in order to manufacture PLA sheet/film with improved flexibility without affecting other package characteristics. Earlier, several multi-step approaches to formulating PLA/ESO blends have been investigated [1, 5]. To achieve this goal, a processing system in which an extruder and a peristaltic injector pump attached in tandem was developed for a continuous and accurate incorporation of the plasticizer into the molten matrix.

The effect of ESO addition levels on impact and tensile properties of plasticized PLA sheets was examined. The flexibility of plasticized specimens and the phase morphology between the plasticizer and the matrix were characterized through glass transition measurement and scanning electron microscopy, respectively. Additionally, this study examined the effect of plasticizer on the heat sealability of PLA film during pouch manufacture by measuring both the burst pressure and seal strength of the flexible pouches sealed at different sealing conditions. Finally, the tensile properties of plasticized PLA blown films as a function of storage time over a span of 125 days was examined. The following conclusions were drawn from the experimental data.

1. The tandem extrusion-injection pump system developed in this study was found to be an effective and efficient approach for a continuous and accurate incorporation of the plasticizer into the molten matrix.



2. The impact strength of the blends remained nearly unchanged up to 5 wt % ESO content and then increased significantly with increasing ESO content. The threshold ESO content at which the transition from brittle-to-ductile behavior in PLA blends occurred was in the range between 5 and 10 wt % ESO content. The impact strength increased significantly from 5 wt % to 10 wt % ESO and reached a maximum at 10 wt % ESO and leveled off with any further addition of ESO.
3. The ductility of plasticized PLA sheets followed similar trends as the impact strength results. Notice that the brittle-to-ductile transition also occurred in the range between 5 and 10 wt % ESO, in agreement with the impact strength results.
4. Both the tensile strength and the modulus of the sheets decreased with increasing content of ESO in the blend. This was expected due to the plasticization effect, which induced a decrease in the glass transition temperature resulting in mobility of the PLA polymer chains.
5. Flexible pouches made of plasticized PLA films failed at a lower burst pressure than their counterparts with unplasticized films, mainly attributable to the plasticizing effect, which lowered the strength of plasticized specimens compared to neat PLA films. The range of sealing temperatures investigated did not influence the burst pressure because the package failed due to material failure while the seals remained intact during burst tests (non peelable seals). The seal strength of pouches made with PLA films was not affected by the addition of plasticizer or by the sealing temperatures studied.

6. Both the ductility and yield strength of films plasticized with 15 wt % ESO tested over a 4 months storage period remained the same with increasing storage time. The results implied that the flexibility of plasticized film did not change over the period of time tested, which indicate the permanence characteristics of ESO in the PLA/ESO blends. In contrast, the tensile modulus showed a slight but a statistically significant increase in stiffness after only 7 storage days, indicating a possible loss of plasticizer from the film as the storage time increased. This contradictory trend will be investigated further.

## **5.2 Future work**

While this study mainly focused on the mechanical properties of the plasticized PLA films and sheets, the effect of ESO content on the barrier properties of plasticized PLA must also be studied for other packaging applications. This study showed possible loss of plasticizer from the film as the storage time increased. It would be appropriate to perform a thorough migration study to gain an in-depth understanding of the permanence/leachability of ESO from plasticized PLA films. Distribution properties such as vibration, impact properties and shock absorption could also be studied for packages designed with ESO-plasticized PLA films.

## REFERENCES

### 5.3 References

1. Baiardo, M., Frisoni, G., Scandola, M., Rimelen, M., Lips, D., Ruffieux, K. and Wintermantel, E., Thermal and mechanical properties of plasticized poly(L-lactic acid), *Journal of Applied Polymer Science*, 90: 1731-1738 (2003).
2. Ljungberg, N. and Wesslen, B., Preparation and properties of plasticized poly(lactic acid) films, *Biomacromolecules*, 6: 1789-1796 (2005).
3. Semba, T., Kitagawa, K., Ishiaku, U.S., and Hamada, H., The effect of crosslinking on the mechanical properties of polylactic acid/polycaprolactone blends, *Journal of Applied Polymer Science*, 101, 1816-1825 (2006).
4. Siracusa, V., Blanco, I., Romani, S., Tylewicz, U., Rocculi, P., and Rosa, M.D., Poly(lactic acid)-modified films for food packaging application: physical, mechanical, and barrier behavior, *Journal of Applied Polymer Science*, 125: E390-E401(2012).
5. Robertson, M.L., Chang, K., Gramlich, W.M., and Hillmyer, M.A., Toughening of polylactide with polymerized soybean oil, *Macromolecules*, 43: 1807-1814 (2010).

## **APPENDICES**

## **APPENDIX I**

### **IMPACT STRENGTH DATA OF PLA SHEETS**

Table A.1 Effect of ESO content on the impact strength of PLA sheets

| <b>ESO content</b> | <b>Impact Strength (J/m)</b> |           |             |            |            |            |
|--------------------|------------------------------|-----------|-------------|------------|------------|------------|
|                    | <b>0%</b>                    | <b>5%</b> | <b>7.5%</b> | <b>10%</b> | <b>15%</b> | <b>20%</b> |
|                    | 19.28                        | 24.07     | 38.65       | 38.45      | 52.73      | 41.17      |
|                    | 18.50                        | 14.72     | 35.07       | 39.02      | 39.78      | 39.40      |
|                    | 24.08                        | 17.06     | 33.08       | 53.47      | 41.81      | 41.01      |
|                    | 5.85                         | 17.43     | 33.80       | 36.87      | 45.68      | 42.10      |
|                    | 13.57                        | 12.90     | 34.96       | 39.24      | 42.34      | 41.47      |
|                    | 15.17                        | 14.81     | 39.78       | 45.81      | 63.49      | 41.18      |
|                    | 16.23                        | 20.73     | 35.98       | 42.67      | 41.68      | 42.99      |
|                    | 13.31                        | 16.20     | 34.96       | 41.08      | 57.97      | 41.59      |
|                    | 15.75                        | 17.24     | 37.09       | 58.70      | 49.92      | 47.13      |
|                    | 15.75                        | 17.24     | 37.22       | 44.94      | 35.62      | 45.80      |
| <b>Avg</b>         | 15.75                        | 17.24     | 36.06       | 44.03      | 47.10      | 42.38      |
| <b>Std</b>         | 4.70                         | 3.18      | 2.12        | 7.07       | 8.78       | 2.35       |

Table A.2. Analysis of variance for the effect of ESO content on the impact strength of PLA

| Source      | Sum of Squares | DF | Mean Square | F Value | Prob > F |             |
|-------------|----------------|----|-------------|---------|----------|-------------|
| Model       | 10,566.64      | 5  | 2,113.33    | 78.90   | < 0.0001 | Significant |
| ESO content | 10,566.64      | 5  | 2,113.33    | 78.90   | < 0.0001 |             |
| Pure Error  | 1,692.98       | 60 | 28.22       |         |          |             |
| Cor Total   | 12,259.62      | 65 |             |         |          |             |

Table A.3. Pairwise comparison of impact strength of PLA/ESO blends

| ESO Content | Mean Difference | DF | Standard Error | t for Ho Coeff = 0 | Prob >  t |
|-------------|-----------------|----|----------------|--------------------|-----------|
| 1 vs 2      | -1.25           | 1  | 2.27           | -0.55              | 0.5818    |
| 1 vs 3      | -19.56          | 1  | 2.27           | -8.64              | < 0.0001  |
| 1 vs 4      | -27.52          | 1  | 2.27           | -12.15             | < 0.0001  |
| 1 vs 5      | -31.36          | 1  | 2.27           | -13.85             | < 0.0001  |
| 1 vs 6      | -27.21          | 1  | 2.27           | -12.01             | < 0.0001  |
| 2 vs 3      | -18.31          | 1  | 2.27           | -8.08              | < 0.0001  |
| 2 vs 4      | -26.26          | 1  | 2.27           | -11.60             | < 0.0001  |
| 2 vs 5      | -30.11          | 1  | 2.27           | -13.29             | < 0.0001  |
| 2 vs 6      | -25.96          | 1  | 2.27           | -11.46             | < 0.0001  |
| 3 vs 4      | -7.96           | 1  | 2.27           | -3.51              | 0.0008    |
| 3 vs 5      | -11.80          | 1  | 2.27           | -5.21              | < 0.0001  |
| 3 vs 6      | -7.65           | 1  | 2.27           | -3.38              | 0.0013    |
| 4 vs 5      | -3.84           | 1  | 2.27           | -1.70              | 0.0950    |
| 4 vs 6      | 0.31            | 1  | 2.27           | 0.14               | 0.8922    |
| 5 vs 6      | 4.15            | 1  | 2.27           | 1.83               | 0.0719    |

ESO Contents: 1 – 0 %, 2 – 5 %, 3 – 7.5 %, 4 – 10 %, 5 – 15 %, and 6 – 20 %



**APPENDIX II**  
**TENSILE PROPERTIES DATA OF PLA SHEETS**

## **APPENDIX II-1**

### **The Effect of ESO Content on the Tensile Modulus of PLA Sheets**

Table A.4 Effect of ESO content on the tensile modulus of PLA sheets

| <b>ESO content</b> | <b>Tensile Modulus (MPa)</b> |           |            |            |            |
|--------------------|------------------------------|-----------|------------|------------|------------|
|                    | <b>0%</b>                    | <b>5%</b> | <b>10%</b> | <b>15%</b> | <b>20%</b> |
|                    | 2,860.73                     | 2,722.15  | 2,353.02   | 2,409.86   | 2,530.32   |
|                    | 2,564.51                     | 2,758.41  | 2,389.90   | 2,087.68   | 2,112.13   |
|                    | 2,686.62                     | 2,613.61  | 2,082.57   | 2,077.50   | 2,274.66   |
|                    | 2,665.25                     | 2,811.13  | 2,446.84   | 2,328.59   | 2,394.28   |
|                    | 2,581.39                     | 2,304.45  | 2,505.97   | 2,296.96   | 1,876.32   |
|                    | 2,335.16                     | 2,394.75  | 2,355.87   | 2,331.35   | 2,269.45   |
|                    | 2,490.15                     | 2,361.11  | 2,497.43   | 2,215.09   | 2,016.55   |
|                    | 2,553.62                     | 2,404.51  | 2,475.10   | 2,273.89   | 2,299.79   |
|                    | 2,594.91                     | 2,591.85  | 2,259.28   | 2,397.66   | 2,034.15   |
|                    | 2,616.25                     | 2,551.33  | 2,340.23   | 2,351.98   | 2,200.85   |
| <b>Average</b>     | 2,594.86                     | 2,551.33  | 2,370.62   | 2,277.06   | 2,200.85   |
| <b>Std Dev</b>     | 135.70                       | 189.83    | 128.37     | 117.06     | 206.42     |

Table A.5. Analysis of variance for the effect of ESO content on the tensile modulus of PLA

| Source      | Sum of Squares | DF | Mean Square | F Value | Prob > F |             |
|-------------|----------------|----|-------------|---------|----------|-------------|
| Model       | 1,165,043      | 4  | 291,260.7   | 12.2892 | < 0.0001 | Significant |
| ESO content | 1,165,043      | 4  | 291,260.7   | 12.2892 | < 0.0001 |             |
| Pure Error  | 1,066,520      | 45 | 23,700.44   |         |          |             |
| Cor Total   | 2,231,563      | 49 |             |         |          |             |

Table A.6. Pairwise comparison of tensile modulus of PLA/ESO blends

| ESO Content | Mean Difference | DF   | Standard Error | t for Ho Coeff = 0 | Prob >  t |
|-------------|-----------------|------|----------------|--------------------|-----------|
| 1 vs 2      | 43.53           | 1.00 | 68.85          | 0.63               | 0.5304    |
| 1 vs 3      | 224.24          | 1.00 | 68.85          | 3.26               | 0.0021    |
| 1 vs 4      | 317.80          | 1.00 | 68.85          | 4.62               | < 0.0001  |
| 1 vs 5      | 394.01          | 1.00 | 68.85          | 5.72               | < 0.0001  |
| 2 vs 3      | 180.71          | 1.00 | 68.85          | 2.62               | 0.0118    |
| 2 vs 4      | 274.27          | 1.00 | 68.85          | 3.98               | 0.0002    |
| 2 vs 5      | 350.48          | 1.00 | 68.85          | 5.09               | < 0.0001  |
| 3 vs 4      | 93.57           | 1.00 | 68.85          | 1.36               | 0.1809    |
| 3 vs 5      | 169.77          | 1.00 | 68.85          | 2.47               | 0.0175    |
| 4 vs 5      | 76.21           | 1.00 | 68.85          | 1.11               | 0.2742    |

ESO Contents: 1 – 0 %, 2 – 5 %, 3 – 10 %, 4 – 15 %, and 5 – 20 %

## **APPENDIX II-2**

### **The Effect of ESO Content on the Tensile Strength at Yield of PLA Sheets**

Table A.7 Effect of ESO content on the tensile strength at yield of PLA sheets

| <b>ESO content</b> | <b>Tensile Strength at Yield (MPa)</b> |           |            |            |            |
|--------------------|--|-----------|------------|------------|------------|
|                    | <b>0%</b>                              | <b>5%</b> | <b>10%</b> | <b>15%</b> | <b>20%</b> |
|                    | 57.74                                  | 61.28     | 36.15      | 30.78      | 26.10      |
|                    | 56.70                                  | 51.94     | 36.19      | 27.97      | 24.48      |
|                    | 56.12                                  | 58.98     | 34.56      | 30.61      | 26.07      |
|                    | 56.69                                  | 62.75     | 39.22      | 28.55      | 29.87      |
|                    | 58.99                                  | 59.01     | 37.65      | 28.53      | 23.91      |
|                    | 58.04                                  | 61.96     | 36.53      | 29.90      | 27.33      |
|                    | 56.09                                  | 61.56     | 36.38      | 31.91      | 28.56      |
|                    | 55.98                                  | 58.22     | 37.40      | 28.33      | 27.43      |
|                    | 57.37                                  | 55.71     | 39.01      | 30.77      | 28.82      |
|                    | 57.19                                  | 59.05     | 36.95      | 30.06      | 27.19      |
| <b>Average</b>     | 57.09                                  | 59.05     | 37.00      | 29.74      | 27.19      |
| <b>Std Dev</b>     | 0.97                                   | 3.46      | 1.39       | 1.32       | 1.69       |

Table A.8. Analysis of variance for the effect of ESO content on the tensile strength at yield of PLA

| Source      | Sum of Squares | DF | Mean Square | F Value | Prob > F | Significant |
|-------------|----------------|----|-------------|---------|----------|-------------|
| Model       | 9,192.416      | 4  | 2,298.104   | 610.024 | < 0.0001 |             |
| ESO content | 9,192.416      | 4  | 2,298.104   | 610.024 | < 0.0001 |             |
| Pure Error  | 169.5254       | 45 | 3.767232    |         |          |             |
| Cor Total   | 9,361.941      | 49 |             |         |          |             |

Table A.9. Pairwise comparison of tensile strength at yield of PLA

| ESO Content | Mean Difference | DF   | Standard Error | t for Ho Coeff = 0 | Prob >  t |
|-------------|-----------------|------|----------------|--------------------|-----------|
| 1 vs 2      | -1.96           | 1.00 | 0.87           | -2.25              | 0.0291    |
| 1 vs 3      | 20.09           | 1.00 | 0.87           | 23.14              | < 0.0001  |
| 1 vs 4      | 27.35           | 1.00 | 0.87           | 31.51              | < 0.0001  |
| 1 vs 5      | 30.11           | 1.00 | 0.87           | 34.69              | < 0.0001  |
| 2 vs 3      | 22.04           | 1.00 | 0.87           | 25.39              | < 0.0001  |
| 2 vs 4      | 29.31           | 1.00 | 0.87           | 33.76              | < 0.0001  |
| 2 vs 5      | 32.07           | 1.00 | 0.87           | 36.95              | < 0.0001  |
| 3 vs 4      | 7.26            | 1.00 | 0.87           | 8.37               | < 0.0001  |
| 3 vs 5      | 10.03           | 1.00 | 0.87           | 11.55              | < 0.0001  |
| 4 vs 5      | 2.77            | 1.00 | 0.87           | 3.19               | 0.0026    |

ESO Contents: 1 – 0 %, 2 – 5 %, 3 – 10 %, 4 – 15 %, and 5 – 20 %.

## **APPENDIX II-3**

### **The Effect of ESO Content on the Ductility of PLA Sheets**



Table A.10 Effect of ESO content on the tensile strain at break and at yield of PLA sheets

|                  | <b>Tensile Strain (%)</b> |              |               |              |                |              |                |              |                |              |
|------------------|---------------------------|--------------|---------------|--------------|----------------|--------------|----------------|--------------|----------------|--------------|
|                  | <b>0% ESO</b>             |              | <b>5% ESO</b> |              | <b>10% ESO</b> |              | <b>15% ESO</b> |              | <b>20% ESO</b> |              |
|                  | <b>Break</b>              | <b>Yield</b> | <b>Break</b>  | <b>Yield</b> | <b>Break</b>   | <b>Yield</b> | <b>Break</b>   | <b>Yield</b> | <b>Break</b>   | <b>Yield</b> |
|                  | 6.25                      | 2.64         | 3.43          | 3.30         | 82.92          | 2.25         | 100.93         | 1.57         | 42.83          | 1.33         |
|                  | 4.94                      | 3.10         | 2.51          | 2.48         | 58.32          | 2.30         | 38.88          | 1.85         | 54.3           | 1.43         |
|                  | 3.4                       | 2.91         | 3.33          | 3.13         | 106.14         | 2.34         | 95.72          | 1.82         | 37.37          | 1.44         |
|                  | 3.33                      | 3.03         | 3.23          | 3.05         | 84.82          | 2.16         | 80.99          | 1.52         | 77.56          | 1.57         |
|                  | 5.95                      | 3.281        | 4.43          | 4.12         | 80.84          | 2.09         | 57.09          | 1.57         | 45.16          | 1.95         |
|                  | 6.77                      | 3.66         | 4.07          | 3.99         | 95.73          | 2.23         | 66.81          | 1.57         | 21.97          | 1.67         |
|                  | 5.07                      | 3.46         | 3.89          | 3.87         | 25.18          | 1.92         | 79.77          | 1.74         | 36.88          | 1.90         |
|                  | 4.59                      | 3.20         | 4.3           | 3.54         | 91.06          | 2.19         | 89.87          | 1.59         | 50.31          | 1.67         |
|                  | 4.54                      | 3.13         | 3.67          | 3.03         | 102.96         | 2.59         | 115.48         | 1.65         | 72.2           | 1.54         |
|                  | 3.69                      | 3.19         | 3.65          | 3.39         | 88.21          | 2.23         | 80.62          | 1.66         | 48.73          | 1.61         |
| <b>Avg</b>       | 4.85                      | 3.16         | 3.65          | 3.39         | 81.62          | 2.23         | 80.62          | 1.66         | 48.73          | 1.61         |
| <b>Std. Dev.</b> | 1.19                      | 0.28         | 0.57          | 0.50         | 23.87          | 0.17         | 22.18          | 0.11         | 16.49          | 0.20         |

Table A.11 Effect of ESO content on the ductility of PLA sheets

| <b>ESO content</b> | <b>Ductility</b> |           |            |            |            |
|--------------------|------------------|-----------|------------|------------|------------|
|                    | <b>0%</b>        | <b>5%</b> | <b>10%</b> | <b>15%</b> | <b>20%</b> |
|                    | 2.37             | 1.04      | 36.89      | 64.09      | 32.23      |
|                    | 1.59             | 1.01      | 25.39      | 20.97      | 38.04      |
|                    | 1.16             | 1.06      | 45.24      | 52.57      | 25.89      |
|                    | 1.10             | 1.06      | 39.17      | 53.09      | 49.25      |
|                    | 1.81             | 1.08      | 38.50      | 36.25      | 23.13      |
|                    | 1.85             | 1.02      | 42.91      | 42.42      | 13.13      |
|                    | 1.46             | 1.00      | 13.12      | 45.87      | 19.38      |
|                    | 1.43             | 1.21      | 41.43      | 56.47      | 30.06      |
|                    | 1.45             | 1.21      | 39.72      | 69.70      | 46.82      |
|                    | 1.15             | 1.08      | 39.54      | 49.05      | 30.88      |
| <b>Average</b>     | 1.54             | 1.08      | 36.19      | 49.05      | 30.88      |
| <b>Std Dev</b>     | 0.39             | 0.07      | 9.67       | 13.91      | 11.44      |

Table A.12. Analysis of variance for the effect of ESO content on the ductility of PLA

| Source      | Sum of Squares | DF | Mean Square | F Value | Prob > F |             |
|-------------|----------------|----|-------------|---------|----------|-------------|
| Model       | 18,530.59      | 4  | 4,632.648   | 55.3916 | < 0.0001 | Significant |
| ESO content | 18,530.59      | 4  | 4,632.648   | 55.3916 | < 0.0001 |             |
| Pure Error  | 3,763.548      | 45 | 83.63441    |         |          |             |
| Cor Total   | 22,294.14      | 49 |             |         |          |             |

Table A.13. Pairwise comparison of ductility of PLA/ESO blends

| ESO Content | Mean Difference | DF   | Standard Error | t for Ho<br>Coeff = 0 | Prob >  t |
|-------------|-----------------|------|----------------|-----------------------|-----------|
| 1 vs 2      | 0.46            | 1.00 | 4.09           | 0.11                  | 0.9108    |
| 1 vs 3      | -34.65          | 1.00 | 4.09           | -8.47                 | < 0.0001  |
| 1 vs 4      | -47.51          | 1.00 | 4.09           | -11.62                | < 0.0001  |
| 1 vs 5      | -29.34          | 1.00 | 4.09           | -7.17                 | < 0.0001  |
| 2 vs 3      | -35.11          | 1.00 | 4.09           | -8.59                 | < 0.0001  |
| 2 vs 4      | -47.97          | 1.00 | 4.09           | -11.73                | < 0.0001  |
| 2 vs 5      | -29.80          | 1.00 | 4.09           | -7.29                 | < 0.0001  |
| 3 vs 4      | -12.86          | 1.00 | 4.09           | -3.14                 | 0.0030    |
| 3 vs 5      | 5.31            | 1.00 | 4.09           | 1.30                  | 0.2008    |
| 4 vs 5      | 18.17           | 1.00 | 4.09           | 4.44                  | < 0.0001  |

ESO Contents: 1 – 0 %, 2 – 5 %, 3 – 10 %, 4 – 15 %, and 5 – 20 %.

## **APPENDIX III**

### **TENSILE PROPERTIES DATA OF PLA FILMS**

## **APPENDIX III-1**

**The Effect of Storage Time on the Tensile Strength at Yield of PLA Films**

**Plasticized with 15 wt % ESO**

Table A.14. Effect of storage time on the tensile strength at yield of plasticized PLA films

| <b>Storage Time</b> | <b>Tensile Strength at Yield (MPa)</b> |               |                |                |                 |
|---------------------|--|---------------|----------------|----------------|-----------------|
|                     | <b>0 days</b>                          | <b>7 days</b> | <b>45 days</b> | <b>92 days</b> | <b>125 days</b> |
|                     | 35.56                                  | 34.50         | 32.07          | 34.51          | 28.45           |
|                     | 31.09                                  | 32.91         | 33.79          | 34.39          | 31.66           |
|                     | 34.29                                  | 38.25         | 32.16          | 34.95          | 32.81           |
|                     | 34.90                                  | 39.52         | 37.55          | 33.35          | 31.77           |
|                     | 30.16                                  | 34.21         | 33.13          | 32.84          | 36.46           |
|                     | 32.87                                  | 35.70         | 33.67          | 37.25          | 31.58           |
|                     | 32.52                                  | 39.40         | 31.90          | 33.19          | 38.57           |
|                     | 36.74                                  | 34.97         | 34.43          | 36.48          | 31.17           |
|                     | 33.91                                  | 28.13         | 32.58          | 30.04          | 34.64           |
|                     | 33.78                                  | 30.78         | 32.51          | 33.60          | 30.00           |
| <b>Average</b>      | 33.58                                  | 34.84         | 33.38          | 34.06          | 32.71           |
| <b>Std Dev</b>      | 1.99                                   | 3.66          | 1.69           | 2.01           | 3.04            |

Table A.15. Analysis of variance for the effect of storage time on the tensile strength at yield of plasticized PLA films

| Source       | Sum of Squares | DF | Mean Square | F Value | Prob > F |                 |
|--------------|----------------|----|-------------|---------|----------|-----------------|
| Model        | 25.13          | 4  | 6.28        | 0.94    | 0.4514   | Not significant |
| Storage time | 25.13          | 4  | 6.28        | 0.94    | 0.4514   |                 |
| Pure Error   | 301.83         | 45 | 6.70        |         |          |                 |
| Cor Total    | 326.96         | 49 |             |         |          |                 |

Table A.16. Pairwise comparison of tensile strength at yield of plasticized PLA films

| ESO Content | Mean Difference | DF   | Standard Error | t for Ho Coeff = 0 | Prob >  t |
|-------------|-----------------|------|----------------|--------------------|-----------|
| 1 vs 2      | -1.25           | 1.00 | 1.16           | -1.08              | 0.2849    |
| 1 vs 3      | 0.20            | 1.00 | 1.16           | 0.17               | 0.8620    |
| 1 vs 4      | -0.48           | 1.00 | 1.16           | -0.41              | 0.6814    |
| 1 vs 5      | 0.87            | 1.00 | 1.16           | 0.75               | 0.4559    |
| 2 vs 3      | 1.46            | 1.00 | 1.16           | 1.26               | 0.2152    |
| 2 vs 4      | 0.77            | 1.00 | 1.16           | 0.67               | 0.5070    |
| 2 vs 5      | 2.12            | 1.00 | 1.16           | 1.83               | 0.0732    |
| 3 vs 4      | -0.68           | 1.00 | 1.16           | -0.59              | 0.5594    |
| 3 vs 5      | 0.67            | 1.00 | 1.16           | 0.58               | 0.5666    |
| 4 vs 5      | 1.35            | 1.00 | 1.16           | 1.17               | 0.2500    |

Storage days: 1 – 0 day, 2 – 7 days, 3 – 45 days, 4 – 92 days, and 5 – 125 days

## **APPENDIX III-2**

### **The Effect of Storage Time on the Tensile Modulus of PLA Films Plasticized with 15 wt % ESO**



Table A.17. Effect of storage time on the tensile modulus of plasticized PLA films

| <b>Storage Time</b> | <b>Tensile Modulus (MPa)</b> |               |                |                |                 |
|---------------------|------------------------------|---------------|----------------|----------------|-----------------|
|                     | <b>0 days</b>                | <b>7 days</b> | <b>45 days</b> | <b>92 days</b> | <b>125 days</b> |
|                     | 2,433.52                     | 2,518.34      | 2,555.18       | 2,702.09       | 2,332.75        |
|                     | 2,281.20                     | 2,295.16      | 2,246.60       | 2,699.53       | 2,411.47        |
|                     | 2,411.76                     | 2,492.07      | 2,480.21       | 2,707.00       | 2,399.35        |
|                     | 2,308.12                     | 2,514.13      | 2,801.84       | 2,668.89       | 2,360.62        |
|                     | 2,107.45                     | 2,377.00      | 2,471.46       | 2,631.10       | 2,902.41        |
|                     | 2,342.31                     | 2,513.23      | 2,507.46       | 2,819.72       | 2,497.61        |
|                     | 2,091.88                     | 2,654.83      | 2,394.79       | 2,387.74       | 2,972.66        |
|                     | 2,395.58                     | 2,412.59      | 2,657.79       | 2,887.82       | 2,572.77        |
|                     | 2,210.09                     | 2,175.37      | 2,423.34       | 2,369.19       | 2,665.57        |
|                     | 2,289.39                     | 2,442.25      | 2,544.21       | 2,616.96       | 2,364.55        |
| <b>Average</b>      | 2,287.13                     | 2,439.50      | 2,508.29       | 2,649.00       | 2,547.98        |
| <b>Std Dev</b>      | 119.5318                     | 133.9929      | 150.0888       | 164.386        | 230.6409        |

Table A.18. Analysis of variance for the effect of storage time on the tensile modulus of plasticized PLA films

| Source       | Sum of Squares | DF | Mean Square | F Value | Prob > F |             |
|--------------|----------------|----|-------------|---------|----------|-------------|
| Model        | 726,191.7      | 4  | 181,547.9   | 6.72466 | 0.0002   | Significant |
| Storage time | 726,191.7      | 4  | 181,547.9   | 6.72466 | 0.0002   |             |
| Pure Error   | 1,214,879      | 45 | 26,997.31   |         |          |             |
| Cor Total    | 1,941,071      | 49 |             |         |          |             |

Table A.19. Pairwise comparison of tensile modulus of plasticized PLA film

| ESO Content | Mean Difference | DF   | Standard Error | t for Ho Coeff = 0 | Prob >  t |
|-------------|-----------------|------|----------------|--------------------|-----------|
| 1 vs 2      | -152.37         | 1.00 | 73.48          | -2.07              | 0.0439    |
| 1 vs 3      | -221.16         | 1.00 | 73.48          | -3.01              | 0.0043    |
| 1 vs 4      | -361.87         | 1.00 | 73.48          | -4.92              | < 0.0001  |
| 1 vs 5      | -260.85         | 1.00 | 73.48          | -3.55              | 0.0009    |
| 2 vs 3      | -68.79          | 1.00 | 73.48          | -0.94              | 0.3542    |
| 2 vs 4      | -209.51         | 1.00 | 73.48          | -2.85              | 0.0066    |
| 2 vs 5      | -108.48         | 1.00 | 73.48          | -1.48              | 0.1468    |
| 3 vs 4      | -140.72         | 1.00 | 73.48          | -1.92              | 0.0619    |
| 3 vs 5      | -39.69          | 1.00 | 73.48          | -0.54              | 0.5918    |
| 4 vs 5      | 101.03          | 1.00 | 73.48          | 1.37               | 0.1760    |

Storage days: 1 – 0 day, 2 – 7 days, 3 – 45 days, 4 – 92 days, and 5 – 125 days

### **APPENDIX III-3**

#### **The Effect of Storage Time on the Energy to Break of PLA Films Plasticized with 15 wt % ESO**

Table A.20. Effect of storage time on the energy at break of plasticized films

| <b>Storage Time</b> | <b>Energy at Break (J)</b> |               |                |                |                 |
|---------------------|----------------------------|---------------|----------------|----------------|-----------------|
|                     | <b>0 days</b>              | <b>7 days</b> | <b>45 days</b> | <b>92 days</b> | <b>125 days</b> |
|                     | 5.79                       | 6.80          | 4.64           | 1.23           | 2.40            |
|                     | 11.94                      | 4.82          | 7.57           | 1.01           | 2.34            |
|                     | 3.27                       | 9.06          | 5.29           | 4.08           | 4.02            |
|                     | 3.44                       | 7.75          | 3.63           | 0.50           | 0.91            |
|                     | 9.24                       | 4.02          | 5.60           | 3.10           | 4.14            |
|                     | 5.81                       | 3.37          | 5.80           | 3.54           | 2.60            |
|                     | 4.32                       | 6.06          | 6.20           | 1.97           | 3.33            |
|                     | 9.04                       | 7.36          | 4.65           | 3.35           | 4.62            |
|                     | 4.37                       | 6.45          | 7.90           | 2.41           | 3.69            |
|                     | 6.35                       | 4.18          | 7.47           | 2.69           | 3.64            |
| <b>Average</b>      | 6.36                       | 5.99          | 5.87           | 2.39           | 3.17            |
| <b>Std Dev</b>      | 2.86                       | 1.85          | 1.42           | 1.19           | 1.11            |

Table A.21. Analysis of variance for the effect of storage time on the energy at break of plasticized PLA films

| Source       | Sum of Squares | DF | Mean Square | F Value | Prob > F |             |
|--------------|----------------|----|-------------|---------|----------|-------------|
| Model        | 8.263008       | 4  | 2.065752    | 12.2568 | < 0.0001 | Significant |
| Storage time | 8.263008       | 4  | 2.065752    | 12.2568 | < 0.0001 |             |
| Pure Error   | 7.584243       | 45 | 0.168539    |         |          |             |
| Cor Total    | 15.84725       | 49 |             |         |          |             |

Table A.22. Pairwise comparison of energy at break of plasticized PLA film

| ESO Content | Mean Difference | DF | Standard Error | t for Ho Coeff = 0 | Prob >  t |
|-------------|-----------------|----|----------------|--------------------|-----------|
| 1 vs 2      | 0.047403        | 1  | 0.183597       | 0.258192           | 0.7974    |
| 1 vs 3      | 0.059688        | 1  | 0.183597       | 0.325102           | 0.7466    |
| 1 vs 4      | 0.976866        | 1  | 0.183597       | 5.320717           | < 0.0001  |
| 1 vs 5      | 0.718153        | 1  | 0.183597       | 3.911581           | 0.0003    |
| 2 vs 3      | 0.012285        | 1  | 0.183597       | 0.06691            | 0.9469    |
| 2 vs 4      | 0.929463        | 1  | 0.183597       | 5.062525           | < 0.0001  |
| 2 vs 5      | 0.67075         | 1  | 0.183597       | 3.653389           | 0.0007    |
| 3 vs 4      | 0.917178        | 1  | 0.183597       | 4.995615           | < 0.0001  |
| 3 vs 5      | 0.658466        | 1  | 0.183597       | 3.586479           | 0.0008    |
| 4 vs 5      | -0.25871        | 1  | 0.183597       | -1.40914           | 0.1657    |

Storage days: 1 – 0 day, 2 – 7 days, 3 – 45 days, 4 – 92 days, and 5 – 125 days

## **APPENDIX III-4**

### **The Effect of Storage Time on the Ductility of PLA Films Plasticized with 15 wt % ESO**

Table A.23. Effect of storage time on the tensile strain at break and at yield of plasticized films

|                      | Tensile Strain (%) |       |        |       |         |       |         |       |          |       |
|----------------------|--------------------|-------|--------|-------|---------|-------|---------|-------|----------|-------|
|                      | 0 Days             |       | 7 Days |       | 45 Days |       | 92 Days |       | 125 Days |       |
|                      | Break              | Yield | Break  | Yield | Break   | Yield | Break   | Yield | Break    | Yield |
|                      | 76.79              | 1.82  | 91.06  | 1.72  | 54.48   | 1.90  | 22.70   | 1.46  | 37.31    | 1.54  |
|                      | 109.15             | 1.94  | 55.17  | 1.76  | 90.93   | 1.80  | 22.35   | 1.48  | 29.49    | 0.60  |
|                      | 43.13              | 1.80  | 113.76 | 1.95  | 76.59   | 1.96  | 65.60   | 1.49  | 70.73    | 2.45  |
|                      | 58.65              | 1.92  | 87.55  | 1.84  | 57.81   | 1.98  | 9.75    | 1.29  | 16.46    | 3.09  |
|                      | 117.96             | 1.80  | 63.79  | 1.80  | 82.06   | 1.95  | 72.81   | 1.36  | 77.52    | 1.78  |
|                      | 63.06              | 1.92  | 52.67  | 1.90  | 79.04   | 1.93  | 61.99   | 2.08  | 42.18    | 2.76  |
|                      | 74.33              | 2.21  | 96.73  | 1.85  | 67.59   | 1.97  | 44.23   | 1.97  | 67.46    | 2.32  |
|                      | 104.64             | 1.97  | 96.44  | 1.84  | 81.07   | 1.96  | 70.73   | 1.38  | 83.94    | 2.05  |
|                      | 46.11              | 2.08  | 73.92  | 1.94  | 99.64   | 1.99  | 51.87   | 1.50  | 64.55    | 1.38  |
|                      | 77.15              | 1.95  | 53.03  | 1.84  | 97.15   | 1.80  | 47.77   | 1.47  | 86.05    | 1.39  |
| <b>Avg</b>           | 77.10              | 1.94  | 78.41  | 1.84  | 78.63   | 1.93  | 46.98   | 1.55  | 57.57    | 1.94  |
| <b>Std.<br/>Dev.</b> | 26.07              | 0.13  | 21.69  | 0.07  | 15.26   | 0.07  | 22.15   | 0.26  | 24.38    | 0.75  |

Table A.24. Effect of storage time on the ductility of plasticized films

| <b>Storage Time</b> | <b>Ductility</b> |               |                |                |                 |
|---------------------|------------------|---------------|----------------|----------------|-----------------|
|                     | <b>0 days</b>    | <b>7 days</b> | <b>45 days</b> | <b>92 days</b> | <b>125 days</b> |
|                     | 42.17            | 52.86         | 28.61          | 15.55          | 24.20           |
|                     | 56.39            | 31.43         | 50.39          | 15.14          | 49.38           |
|                     | 23.90            | 58.28         | 39.17          | 43.94          | 28.82           |
|                     | 30.56            | 47.65         | 29.19          | 7.56           | 5.32            |
|                     | 65.37            | 35.35         | 42.06          | 53.43          | 43.48           |
|                     | 32.85            | 27.68         | 40.85          | 29.74          | 15.28           |
|                     | 33.56            | 52.19         | 34.31          | 22.44          | 29.13           |
|                     | 53.15            | 52.49         | 41.46          | 51.30          | 40.95           |
|                     | 22.13            | 38.19         | 49.99          | 34.62          | 46.65           |
|                     | 39.64            | 28.86         | 53.84          | 32.42          | 61.79           |
| <b>Average</b>      | 39.97            | 42.50         | 40.99          | 30.61          | 29.72           |
| <b>Std Dev</b>      | 14.34            | 11.42         | 8.67           | 15.67          | 17.07           |



Table A.25. Analysis of variance for the effect of storage time on the ductility of plasticized PLA films

| Source       | Sum of Squares | DF | Mean Square | F Value | Prob > F |                 |
|--------------|----------------|----|-------------|---------|----------|-----------------|
| Model        | 795.489        | 4  | 198.8722    | 1.63055 | 0.1884   | Not significant |
| Storage time | 795.489        | 4  | 198.8722    | 1.63055 | 0.1884   |                 |
| Pure Error   | 4,268.818      | 35 | 121.9662    |         |          |                 |
| Cor Total    | 5,064.307      | 39 |             |         |          |                 |

Table A.26. Pairwise comparison of ductility of plasticized PLA films

| ESO Content | Mean Difference | DF   | Standard Error | t for Ho Coeff = 0 | Prob >  t |
|-------------|-----------------|------|----------------|--------------------|-----------|
| 1 vs 2      | -4.03           | 1.00 | 5.52           | -0.73              | 0.4706    |
| 1 vs 3      | -1.90           | 1.00 | 5.52           | -0.34              | 0.7328    |
| 1 vs 4      | 8.38            | 1.00 | 5.52           | 1.52               | 0.1379    |
| 1 vs 5      | 4.29            | 1.00 | 5.52           | 0.78               | 0.4422    |
| 2 vs 3      | 2.13            | 1.00 | 5.52           | 0.39               | 0.7024    |
| 2 vs 4      | 12.41           | 1.00 | 5.52           | 2.25               | 0.0310    |
| 2 vs 5      | 8.32            | 1.00 | 5.52           | 1.51               | 0.1409    |
| 3 vs 4      | 10.28           | 1.00 | 5.52           | 1.86               | 0.0710    |
| 3 vs 5      | 6.19            | 1.00 | 5.52           | 1.12               | 0.2698    |
| 4 vs 5      | -4.09           | 1.00 | 5.52           | -0.74              | 0.4636    |

Storage days: 1 – 0 day, 2 – 7 days, 3 – 45 days, 4 – 92 days, and 5 – 125 days

## **APPENDIX IV**

### **BURST PRESSURE AND SEAL STRENGTH DATA OF PLA FILMS**

## **APPENDIX IV-1**

### **Effect of Sealing Temperature on the Burst Pressure of PLA Films**

Table A.27. Effect of sealing temperature on the burst pressure of unplasticized and plasticized films

|                    | Unplasticized PLA |                 |                 | Plasticized PLA |                 |                 |
|--------------------|-------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                    | 100-120<br>(°C)   | 100-135<br>(°C) | 100-150<br>(°C) | 100-120<br>(°C) | 100-135<br>(°C) | 100-150<br>(°C) |
|                    | 61,539            | 70,920          | 66,217          | 38,596          | 35,784          | 37,202          |
|                    | 65,396            | 67,461          | 69,129          | 39,666          | 41,731          | 44,269          |
|                    | 71,990            | 69,054          | 69,228          | 41,905          | 39,715          | 42,254          |
| <b>Avg</b>         | 66,308            | 69,145          | 68,191          | 40,056          | 39,077          | 41,242          |
| <b>Std<br/>Dev</b> | 5,286             | 1,731           | 1,711           | 1,689           | 3,025           | 3,641           |

Table A.28. Analysis of Variance for the effect of sealing temperature and plasticization on the burst pressure PLA films

| Source              | Sum of Squares | DF | Mean Square | F Value | Prob > F |             |
|---------------------|----------------|----|-------------|---------|----------|-------------|
| Model               | 3.49E+09       | 5  | 6.97E+08    | 70.78   | < 0.0001 | Significant |
| Sealing temperature | 3.49E+09       | 5  | 6.97E+08    | 70.78   | < 0.0001 |             |
| Pure Error          | 1.18E+08       | 12 | 9,851,038   |         |          |             |
| Cor Total           | 3.6E+09        | 17 |             |         |          |             |

Table A.29. Pairwise comparison of burst pressure of PLA films

| ESO Content | Mean Difference | DF   | Standard Error | t for Ho Coeff = 0 | Prob >  t |
|-------------|-----------------|------|----------------|--------------------|-----------|
| 1 vs 2      | -2,836.67       | 1.00 | 2,562.69       | -1.11              | 0.2900    |
| 1 vs 3      | -1,883.00       | 1.00 | 2,562.69       | -0.73              | 0.4766    |
| 1 vs 4      | 26,252.67       | 1.00 | 2,562.69       | 10.24              | < 0.0001  |
| 1 vs 5      | 27,231.67       | 1.00 | 2,562.69       | 10.63              | < 0.0001  |
| 1 vs 6      | 25,066.67       | 1.00 | 2,562.69       | 9.78               | < 0.0001  |
| 2 vs 3      | 953.67          | 1.00 | 2,562.69       | 0.37               | 0.7163    |
| 2 vs 4      | 29,089.33       | 1.00 | 2,562.69       | 11.35              | < 0.0001  |
| 2 vs 5      | 30,068.33       | 1.00 | 2,562.69       | 11.73              | < 0.0001  |
| 2 vs 6      | 27,903.33       | 1.00 | 2,562.69       | 10.89              | < 0.0001  |
| 3 vs 4      | 28,135.67       | 1.00 | 2,562.69       | 10.98              | < 0.0001  |
| 3 vs 5      | 29,114.67       | 1.00 | 2,562.69       | 11.36              | < 0.0001  |
| 3 vs 6      | 26,949.67       | 1.00 | 2,562.69       | 10.52              | < 0.0001  |
| 4 vs 5      | 979.00          | 1.00 | 2,562.69       | 0.38               | 0.7091    |
| 4 vs 6      | -1186.00        | 1.00 | 2,562.69       | -0.46              | 0.6518    |
| 5 vs 6      | -2165.00        | 1.00 | 2,562.69       | -0.84              | 0.4147    |

Storage days: 1 – 100-120 Neat PLA film, 2 – 100-135 Neat PLA film, 3 – 100-150 Neat PLA film, 4 – 100-120 Plasticized PLA film, 5 – 100-135 Plasticized PLA film, and 6 – 100-150 Plasticized PLA film

## **APPENDIX IV-2**

### **Effect of Sealing Temperature on the Seal Strength of PLA Films**

Table A.30. Effect of sealing temperature on the seal strength of unplasticized films

|                | Sealing Temperature (°C) |                           |                           |                   |                           |                           |                   |                           |                           |
|----------------|--------------------------|---------------------------|---------------------------|-------------------|---------------------------|---------------------------|-------------------|---------------------------|---------------------------|
|                | 100-120                  |                           |                           | 100-135           |                           |                           | 100-150           |                           |                           |
|                | Max Load<br>(lbf)        | Tensile Extension<br>(in) | Seal Strength<br>(lbf/in) | Max Load<br>(lbf) | Tensile Extension<br>(in) | Seal Strength<br>(lbf/in) | Max Load<br>(lbf) | Tensile Extension<br>(in) | Seal Strength<br>(lbf/in) |
|                | 8.00                     | 0.14                      | 57.15                     | 8.00              | 0.14                      | 57.15                     | 9.00              | 0.16                      | 56.25                     |
|                | 7.00                     | 0.12                      | 58.34                     | 9.00              | 0.16                      | 56.25                     | 6.00              | 0.10                      | 60.01                     |
|                | 6.00                     | 0.10                      | 59.99                     | 8.00              | 0.14                      | 57.15                     | 4.00              | 0.06                      | 66.66                     |
|                | 7.00                     | 0.12                      | 58.34                     | 8.00              | 0.14                      | 57.15                     | 5.00              | 0.08                      | 62.49                     |
|                | 8.00                     | 0.14                      | 57.15                     | 9.00              | 0.16                      | 56.25                     | 6.00              | 0.10                      | 60.73                     |
|                | 8.00                     | 0.14                      | 57.15                     | 9.00              | 0.16                      | 56.25                     | 4.00              | 0.06                      | 66.67                     |
|                | 8.00                     | 0.14                      | 57.15                     | 9.00              | 0.16                      | 56.25                     | 5.00              | 0.07                      | 68.67                     |
|                | 8.00                     | 0.14                      | 57.15                     | 9.00              | 0.16                      | 56.25                     | 9.00              | 0.16                      | 56.25                     |
|                | 8.00                     | 0.14                      | 57.15                     | 7.00              | 0.12                      | 58.34                     | 8.00              | 0.14                      | 57.15                     |
|                | 8.00                     | 0.14                      | 57.15                     | 9.00              | 0.16                      | 56.25                     | 8.00              | 0.14                      | 57.14                     |
| <b>Avg</b>     | 7.60                     | 0.13                      | 57.67                     | 8.50              | 0.15                      | 56.73                     | 6.40              | 0.11                      | 61.20                     |
| <b>Std Dev</b> | 0.70                     | 0.01                      | 0.96                      | 0.71              | 0.01                      | 0.71                      | 1.96              | 0.04                      | 4.72                      |

Table A.31. Effect of sealing temperature on the seal strength of plasticized films

|                | Sealing Temperature (°C) |                        |                        |                |                        |                        |                |                        |                        |
|----------------|--------------------------|------------------------|------------------------|----------------|------------------------|------------------------|----------------|------------------------|------------------------|
|                | 100-120                  |                        |                        | 100-135        |                        |                        | 100-150        |                        |                        |
|                | Max Load (lbf)           | Tensile Extension (in) | Seal Strength (lbf/in) | Max Load (lbf) | Tensile Extension (in) | Seal Strength (lbf/in) | Max Load (lbf) | Tensile Extension (in) | Seal Strength (lbf/in) |
|                | 10.00                    | 0.18                   | 55.56                  | 8.00           | 0.14                   | 57.15                  | 10.00          | 0.18                   | 55.56                  |
|                | 10.00                    | 0.18                   | 55.56                  | 10.00          | 0.18                   | 55.56                  | 7.00           | 0.12                   | 58.34                  |
|                | 8.00                     | 0.14                   | 57.15                  | 10.00          | 0.14                   | 71.43                  | 7.00           | 0.12                   | 58.34                  |
|                | 10.00                    | 0.18                   | 55.56                  | 11.00          | 0.20                   | 55.00                  | 8.00           | 0.14                   | 57.15                  |
|                | 7.00                     | 0.12                   | 58.34                  | 10.00          | 0.18                   | 55.56                  | 6.00           | 0.08                   | 74.99                  |
|                | 8.00                     | 0.14                   | 57.15                  | 10.00          | 0.18                   | 55.56                  | 9.00           | 0.16                   | 56.25                  |
|                | 10.00                    | 0.18                   | 55.56                  | 9.00           | 0.16                   | 56.25                  | 10.00          | 0.18                   | 55.56                  |
|                | 10.00                    | 0.18                   | 55.56                  | 10.00          | 0.18                   | 55.56                  | 10.00          | 0.18                   | 55.56                  |
|                | 8.00                     | 0.14                   | 57.15                  | 7.00           | 0.12                   | 58.34                  | 6.00           | 0.10                   | 60.00                  |
|                | 11.00                    | 0.20                   | 55.00                  | 10.00          | 0.18                   | 55.56                  | 9.00           | 0.16                   | 56.25                  |
| <b>Avg</b>     | 9.20                     | 0.16                   | 56.26                  | 9.50           | 0.17                   | 57.60                  | 8.20           | 0.14                   | 58.80                  |
| <b>Std Dev</b> | 1.32                     | 0.03                   | 1.09                   | 1.18           | 0.03                   | 4.96                   | 1.62           | 0.04                   | 5.88                   |



Table A.32. Analysis of variance for the effect of sealing temperature and plasticization on the seal strength PLA films

| Source              | Sum of Squares | DF | Mean Square | F Value | Prob > F |                 |
|---------------------|----------------|----|-------------|---------|----------|-----------------|
| Model               | 1.177442       | 5  | 0.235488    | 0.68634 | 0.6358   | Not significant |
| Sealing temperature | 1.177442       | 5  | 0.235488    | 0.68634 | 0.6358   |                 |
| Pure Error          | 18.5277        | 54 | 0.343106    |         |          |                 |
| Cor Total           | 19.70514       | 59 |             |         |          |                 |

Table A.33. Pairwise comparison of seal strength of PLA films

| ESO Content | Mean Difference | DF   | Standard Error | t for Ho Coeff = 0 | Prob >  t |
|-------------|-----------------|------|----------------|--------------------|-----------|
| 1 vs 2      | 0.16            | 1.00 | 0.26           | 0.63               | 0.5317    |
| 1 vs 3      | 0.03            | 1.00 | 0.26           | 0.10               | 0.9201    |
| 1 vs 4      | 0.25            | 1.00 | 0.26           | 0.94               | 0.3492    |
| 1 vs 5      | 0.01            | 1.00 | 0.26           | 0.05               | 0.9614    |
| 1 vs 6      | -0.20           | 1.00 | 0.26           | -0.76              | 0.4531    |
| 2 vs 3      | -0.14           | 1.00 | 0.26           | -0.53              | 0.5992    |
| 2 vs 4      | 0.08            | 1.00 | 0.26           | 0.31               | 0.7540    |
| 2 vs 5      | -0.15           | 1.00 | 0.26           | -0.58              | 0.5638    |
| 2 vs 6      | -0.36           | 1.00 | 0.26           | -1.39              | 0.1717    |
| 3 vs 4      | 0.22            | 1.00 | 0.26           | 0.84               | 0.4026    |
| 3 vs 5      | -0.01           | 1.00 | 0.26           | -0.05              | 0.9586    |
| 3 vs 6      | -0.22           | 1.00 | 0.26           | -0.86              | 0.3955    |
| 4 vs 5      | -0.23           | 1.00 | 0.26           | -0.90              | 0.3743    |
| 4 vs 6      | -0.45           | 1.00 | 0.26           | -1.70              | 0.0948    |
| 5 vs 6      | -0.21           | 1.00 | 0.26           | -0.80              | 0.4247    |

Storage days: 1 – 100-120 Neat PLA film, 2 – 100-135 Neat PLA film, 3 – 100-150 Neat PLA film, 4 – 100-120 Plasticized PLA film, 5 – 100-135 Plasticized PLA film, and 6 – 100-150 Plasticized PLA film