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Reactive Extrusion of biodegradable Poly (lactic acid) and Polyester blends:

Effects of PLA/EB062 ratio, Miscibility and Thermal Behavior

by

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Submitted to the Graduate Faculty as partial fulfillment of the requirements for the

Master of Science Degree in Chemical Engineering

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An Abstract of

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In order to reduce carbon footprint in polymers used for packaging and other engineering applications, biobased polymers can be blended with other thermoplastic polymers. The approach in this research was to blend a biobased polymer with a thermoplastic material by extrusion utilizing twin screw extruder. The materials of the choices were biobased polymer polylactic acid (PLA) polymer and extrudable polyester, EB062. This polymer is a branched version of a highly modified CHDM (1, 4cyclohexanedimethanol) copolymer of PET, which is commercially available from Eastman Chemical Company. The objective of this research was to develop means of incorporating biobased content into thermoplastic material and to develop an understanding of the method of variables, the melt process ability, the structure of the resulting blends, and their physical properties.

Differential scanning calorimetry (DSC) was used to study thermal properties. It was observed that two glass transition temperatures appeared when the percentage of PLA involved in the blend was above 20 wt%, regardless of what the viscosity of PLA resins

were used. However, compared with the low viscosity PLA resins, the high viscosity PLA resins showed better compatibility with EB062 at the same operation conditions. It was also observed that, in spite of the operation temperature to prepare the blend, there were no significant changes in glass transition temperatures (T_g) of the blends compared to neat PLA or EB062. With a concern that less residual time during extrusion would limit the chemical reaction between the components of the binary blend, annealing tests were applied. After analysis of the data, it was found that with the increasing annealing time, the crystallization temperature increased, while, the crystallinity decreased. The same trait was observed with the neat PLAs, both high IV resins and low IV resins. A possible reason was that PLA copolymer probably would undergo racemization to form meso-lactide, and therefore impact the material properties of the resulting PLA polymer.

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Chapter 1 Introduction

There is need to reduce carbon footprint in polymers used for packaging and other engineering applications. The methods used include: synthesis of new biobased material, synthesis of copolymers, and blending of biobased polymer with thermoplastic polymers. The approach in this research was to blend a biobased polymer with a thermoplastic polymer by reactive extrusion utilizing a twin screw extruder. The materials of choices were biobased polymer polylactic acid (PLA) and extrudable polyester, EB062. The objective of this research was to develop means of incorporating a biobased content into a thermoplastic material. The choice of the polyester was based on its utilization in extrusion blow molding which intends for a large size container. This research was performed with the anticipation that a copolymer to be formed by a transesterification reaction, since EB062 and PLA contain end groups capable of reacting to form a copolymer. The specific objectives were to study and determine:

- The possibility of forming a copolymer by reaction, which may occur between PLA and polyester through extrusion.
- 2. The effects of time and temperature during melting blending on the reaction.
- 3. The thermal transitions and the crystallization of the blend.

1.1 Introduction to PLA and EB062

1.1.1 Properties and application of Poly (lactic acid) (PLA)

Nowadays, non-renewable crude oil and natural gas are the main resources for deriving plastics. Despite the fact that some plastics are being recycled and reused, the majority are disposed in landfills. The production and use of bioplastics is generally regarded as a more sustainable activity when compared with thermoplastic production from petroleum, because they are less dependent on fossil fuel. Development of consumer products from biodegradable and renewable materials is drawing an increasing attention from researchers and industry [1-5].

Poly (lactic acid) (PLA) is a kind of linear aliphatic polyester derived from renewable sources such as starch and sugar. PLA is environmentally biodegradable and can ultimately be decomposed into carbon dioxide and water [6-7]. The basic building block of PLA, lactic acid (see Figure 1-1), can be produced by carbohydrate fermentation or chemical synthesis. It exists in two optically active configurations, the L- and D- isomers.



Figure 1-1 Chemical structure of L- and D-lactic acid [2]

Polylactide is one of the few polymers in which the stereochemical structure can easily be modified by polymerizing a controlled ratio of the L- or D-isomers. PLA exists in three stereoforms: poly (L-lactide) (L-PLA), poly (D-lactide) (D-PLA), and poly (DL-lactide) (DL-PLA). L-PLA and D-PLA are semi-crystalline, but DL-PLA is more amorphous due to a random distribution of both isomeric forms of lactic acid. PLA will undergo thermal degradation at temperatures above 200°C by hydrolysis, lactide reformation, oxidative main chain scission, and inter- or intramolecular transesterification reactions. PLA degradation is not only dependent on time, and temperature, but also on low-molecular-weight impurities, and catalyst concentration [11]. Polylactide homopolymers have a glass-transition and melt temperature of about 55°C and 175°C, respectively. The required processing temperatures are around 185-190°C [11]. Above these temperatures, unzipping and chain scission reactions will lead to loss of molecular weight, as well as thermal degradations.

1.1.2 Properties and application of EB062

Polymer resins, such as PET, are widely used in the packaging industry. PET is a linear, thermoplastic polyester resin. The numerous advantages of PET include toughness, clarity, lightweight, good barrier properties and good shelf-life performance. Furthermore, PET is recyclable and thus it is environmentally friendly. These characteristics of PET make it a popular material in the manufacturing of food packaging, textile fibers, bottle containers, engineering plastics in automobiles and electronics [12-15].

Eastar Copolyester EB062 is a branched version of a highly modified CHDM (1, 4cyclohexanedimethanol) copolymer of PET having an intrinsic viscosity of 0.75 dl/g sees Figure 1-2,



Figure 1-2 Chemical structure of EB062 [17]

EB062 is a resin specifically developed for extrusion blow molded bottles. Compared to commonly used materials, Eastar copolyester EB062 runs on most standard processing equipment. Branching effectively increases the melt strength of the resin.[18]. Copolymer used in this resin suppresses crystallization producing high clarity at the same time allowing the resin to be processed at lower temperatures. Lower processing temperature results in higher melt viscosity, which in turn serves to improve the process stability in extrusion blow molding. All of these superior characteristics make this resin an excellent choice when manufacturing large bottles.

1.2 PLA/EB062 Blends

1.2.1 Why blends?

Now it has been a common practice to blend existing polymers to obtain new materials. Compared with searching for new monomers and polymers, blending is often done at lower-cost and more time saving. However, simply blending with different polymers most probably leads to a material with poor mechanical properties because of the thermodynamically immiscible of polymer pairs. Compatibilization is therefore called upon. Its role is to stabilize the morphology and modify the interfacial properties of the blend. This is achieved by adding or creating in situ, during the blending process, a third component, often called an interfacial agent, emulsifier or compatibilizer [19]. The latter can be a block or graft copolymer, which tends to be placed at the interfaces between the phases of the blend. As such, the dispersion of one component in the other improved, the interfacial tension is reduced and the adhesion of the interfaces enhanced. The presence of a copolymer also accelerates the melting of polymer blends [19].

1.2.2 Important concerns for PLA/EB062 blends

The greatest concern during blending is to achieve miscibility between the polymer components. The majority of polymer pairs are thermodynamically immiscible because of the positive free energy change (ΔG) during mixing. The properties of the blends are to a large extent relying on the miscibility of the polymers. Weak adhesion at the interface will result in poor mechanical properties such as low impact resistance and low elongation. PLA/EB062 blends are inherently immiscible and opaque parts when insufficient miscibility between these two polymers is achieved. The lack of clarity is due to the particle size of the dispersed phase being large enough to scatter the incident light. Only when the sufficient miscibility between the two phases is achieved can a polymer be transparent. A variety of methods are available to improve the compatibility between components in polymer blends. The principle of the reactive compatibilization of

polymer blends is to use block or random copolymers, containing segments with chemical structures similar to those of polymers in the blend. The copolymers can be added to the mixture of polymers or formed in situ between the functional groups in the polymers [15]. These copolymers act as compatibilizing agents and decrease the surface energy thus inducing compatibilization in the system. More detailed discussion is presented in the literature review section.

In polyester blends, such as PLA/EB062 blends, the transesterification reaction between the two polyesters could produce the required copolymers to increase their compatibility. Most of the research on the transesterification reaction and its effect on miscibility in polymer blends have focused on melt mixing. It was found that temperature and time were the main factors controlling the reactions in the melt phase [22]. In order to achieve adequate transesterification reactions in the blend, the melt mixing process need to be operated either for a longer residence time at moderate temperatures or at comparatively high temperatures.

1.3 Objectives

At Polymer Institute we have ongoing programs that include the development of polymer binary blends of the type A/B, prepared through reactive extrusion. This work has included polyester/polyester as well as polyester/polyamide blend. It is the objective of this program to investigate reactive extrusion blending of biobased polymers with polyesters. For this purpose biobased PLA and an amorphous (slow crystallization, slow melting) polyester were chosen for initial investigations. Specifically Eastman EB062 copolyester was chosen to represent polyester portion of the blend.

The objective of this project was to investigate the thermal properties of a binary polymer blend prepared by extrusion, including the glass transition temperature, the crystallization temperature, the melting temperature, and the crystallization behavior. The results of the analysis of the data will prove the presence of thermal properties changes in the two polymers chosen for the study. A second objective was to develop an understanding of the annealing time at high temperature and various temperatures' effect to PLA/EB062 blends. The experimental variables included: reaction extrusion temperature, PLA correlation in the blend, annealing time, and initial I.V.

Chapter 2 Literature Review

2.1 Properties of Poly (ethylene terephthalate) (PET)

PET is a key member of the synthetic polyester family and of significance in industrial applications. PET was first prepared in 1941 in Accrington U.K. During the last seven decades, PET has found itself in commercial markets for a variety of applications such as textiles, films, foamed articles, and containers for various beverage products such as carbonated soft drinks, water, and fruit juices [23].

The significant success of PET is due to its low manufacturing costs combined with its superb balance of properties that include high optical clarity, high impact strength, gaseous barrier, thermal resistance, ability to strain induced crystallization, good environmental safety and creep resistance. [23].

PET is semi-crystalline aromatic polyester. Depending on the fabrication methods and conditions, PET can be made into amorphous or crystalline forms. PET has a glass transition temperature (T_g) of around 80 °C and melting peak temperature (T_m) of around 255°C[24-25].

2.2 Properties of Poly (ethylene terephthalate) glycol (PETG)

PETG, an amorphous copolymer of PET, is another important polymer in the polymer processing industry. The letter G refers to the additional glycol group along the backbone of the copolymerizing agent, poly (1, 4-cyclohexylenedimethylene terephthalate) (PCT) (see Figures 2-1 and 2-2).



Figure 2-1 chemical structure of PET



Figure 2-2 chemical structure of PCT

The glass-like clarity, toughness and excellent gas-barrier properties make PETG an outstanding choice for storing biologicals. PETG is often used to produce large thermoformed parts such as medical device packaging and face shields. PETG and PET

are very difficult to distinguish because they have similar glass transition temperatures, and they both show relatively similar deformation behavior. But there is a significant difference: PET willingly undergoes strain-induced crystallization, whereas in PETG crystallization is very difficult, if not impossible, at processing temperatures.

2.3 Properties of branched PETG

As mentioned above, PET has widely been used for packaging industry. PET is a popular material in the manufacturing of containers, for example, beverage bottles. There is a requirement for the resins to form beverage bottles. The typically used "bottle grade" PET should have an inherent viscosity (I.V.) of about 0.72-0.84 dl/g. However the bottle grade PET cannot be used to make larger containers such as handle ware by extrusion blow molding because PET has linear polymer chains, which would lead to poor melt strength. Poor melt strength results in the failure to form a parison. The molten parison is drawn down by its own weight, leading in to sagging and failure to form the parison.

An alternate solution is to use branched PETG. An example is the Eastar Copolyester EB062, manufactured by Eastman Chemical Company. EB062 is a branched version of a highly modified CHDM (1, 4-Cyclohexanedimethanol) copolymer of PET having an I.V. of 0.75 dl/g. The melt strength of the resin effectively increases due to branching effect. Copolymer suppresses crystallization producing high clarity while allowing the resin to be operated at lower temperatures.

2.4 Blends of PLA with other materials

Examples of blends of PLA with other materials have been discussed in the literature. Ohkoshi et al. [28] and Koyama and Doi [29] studied the miscibility of binary blends of poly [(R)-3-hydroxybutyric acid] (P [(R)-3HB]) with poly [(S)-lactic acid] (P [(S)-LA]) of various molecular weights. After the DSC analysis, the result showed the blends of P [(R)-3HB] with P [(S)-LA] of M_w values over 20,000 showed two phases, while the blends of P [(R)-3HB] with P [(S)-LA] of M_w values below 18,000 were miscible in the melt over the whole composition range. This revealed that the structure of P [(R)-3HB]/ P [(S)-LA] blends was strongly dependent on the molecular weight of the P [(S)-LA] component.

Suyatma et al. [30] reported on biodegradable film blends of chitosan with PLA by solution mixing and film casting. Incorporating PLA with chitosan would improve the water barrier properties and decrease the water sensitivity of chitosan film, because the chitosan is a natural polymer, non-toxic, edible, end biodegradable, and derived by deacetylation of chitin. The elastic modulus and tensile strength of chitosan, however, decreased due to the addition of PLA. Thermal and mechanical properties revealed that PLA blends and chitosan are incompatible due to absence of specific interaction between PLA and chitosan.

Ke and Sun [31] characterized blends made from starch and PLA in the presence of various water contents. They discovered that the moisture content did not affect the thermal and crystallization properties of PLA in the blend. And the detailed thermal

behaviors of the starch/PLA blends have been studied by DSC. Starch affected the melting point and degree of crystallinity of PLA, and also increased the crystallization rate of PLA.

Jagjit R Khurma, David R Rohindra and Ranjani Devi [32] studied Poly(lactic acid)(PLA)/Poly(vinyl butyral)(PVB) blend prepared through solution casting method using chloroform as solvent. DSC measurements showed that the T_g of PLA and PVB in the blends were almost constant over the entire composition range indicating immiscibility of the polymers. The addition of PVB did not affect the crystallization process and the percentage crystallinity of PLA. They also found a double peak appeared around 162 °C and 168°C for pure PLA and blends containing more than 50 wt% PLA. DSC thermograms are showed in Figure 2-3. These double peaks indicate two populations of crystals with different lamellar thickness when the sample is cooled from the molten state [30].



Figure 2-3 Second-heating-scan DSC thermograms [30].

Y. Hu, Y.S. Hu and V. Topolkaraev et al.[33] performed their research on the crystallization and phase separation in blends of high stereoregular poly(lactide) with poly(ethylene glycol). They determined that blending with PEG can accelerate PLA crystallization. However, the extent of PLA crystallization was depended on the cooling rate. The crystallization temperature of PLA decreased without affecting the extent of PLA crystallization. The crystallization temperature of PEG slightly decreased, while the amount of PEG crystallinity decreased more than in proportion to the amount of PEG to the extent that no crystallization of PEG was detected in the 90/10 blend.

Peng zhao et al. [34] melt blended poly (butylenes adipate-co-butylene terephthalate) (PBAT)/PLA. The blend of PLA and PBAT was prepared using a twin screw extruder. The thermal properties of PLA/PBAT blends were investigated by DSC. The results showed that the T_g of blends did not change with PBAT contents in blends. This trend suggests that the PLA and PBAT are not thermodynamic compatible, especially with

higher PBAT content. The addition of PBAT to the PLA matrix resulted in weaker and wider crystallization peak (about 110°C), suggesting that blending of PBAT with PLA has an influence on crystallizability of PLA. Moreover, T_ms of blends (about 150°C) are the same as T_m of pure PLA, revealing that addition of PBAT into PLA has no effect on T_m of PLA. Additionally, with the increase of PBAT content in blends, Δ Hc and Δ Hm of blends increase firstly, reach the highest value when the PBAT content is 15wt%, and then decrease.

Tadashi Yolohara and Masayuki Yamaguchi [35] studied the structure and properties of binary blends composed of poly (lactic acid) (PLA) and poly (butylenes succinate) (PBS). The rheological measurements in the molten state reveal that the entanglement molecular weight of PLA is lower than that of PBS. Thermal analysis showed that addition of PBS enhances the crystallization of PLA even though PBS is in a molten state. Further, the cold-crystallization for quenched blends occurs at lower temperature than that for a quenched PLA. They concluded that the nucleating ability of PBS leads into generation of PLA crystallites during the quenched operation.

Amita Bhatia, Rahul K. Gupta et al. [36] also studied the compatibility of biodegradable poly (lactic acid) (PLA) and poly (butylenes succinate) (PBS) blends. They concluded that up to 10 wt% of PBS in PLA, T_g and T_m of PLA have not changed, while as the composition of the PBS content increases (> 10 wt%) the thermogram showed a small exothermal peak shift towards lower temperature and continues for other blends. The increase in the PLA content in PLA/PBS blends also showed exothermal peak shifts in the blends are not so noticeable, which indicates immiscibility. Miscibility of PBS in PLA is possible up to 20 wt%. It was reported by Sweet and Bell (1972) and Roberts (1970) that blends of PLA and PBS also show double endothermic peaks in the differential scanning calorimetry (DSC) thermogram for the second heating. It was concluded by these researchers that PLA/PBS blends are immiscible. Lee and Lee (2005) provided reason for the appearance of double endothermic peaks in the second heating scan. They concluded that the appearances of double endothermic peaks are due to quenching after the first heating cycle. It does not give sufficient time for high melting crystallite to form. Therefore, more smaller crystallites are produced.

Abdellatif Mohamed et al. [37] investigated poly (lactic acid)/polystyrene bioblends. From the DSC data, they considered that some type of interaction exists between the polymers because the bioblends displaced T_m and T_c values that varied with composition. On the other hand, these observations were (a) PLA/PS bioblends showed two composition independent glass transitions, and (b) PLA/PS bioblends showed Δ Hc and Δ Hm values that had a linear relation to concentration of PS. Observations of another set of DSC data indicated PLA/PS immiscibility.

M.E. Broz, D.L. VanderHart, N.R. Washburn [36] studied the structure and thermal properties of poly(D,L-lactic acid)/poly(ε -caprolactone) blends. They claimed the two components of PLA/PCL blend are not miscible and some adhesion might happen at the PLA/PCL interface when the majority phase is PCL but not when it is PLA. They concluded that the blend may have complex phase behavior that depends on the method of preparation because the DSC results were somewhat variable.

Maria Letizia Focarete and Mariastella Scandola [37] used a solvent casting method to prepare poly (L-lactide-co-glycolide) (PLLAGA)/poly(3-hydroxybutyrate) (PHB) and

poly(DL-lactide) (PDLLA)/ poly(3-hydroxybutyrate) (PHB) blend films. In their miscibility study, they found that the a-PHB/PDLLA blends are miscible over the whole composition range. However, blends of a-PHB with PLLAGA copolymers containing 5 and 16 mol % of GA units show limited miscibility. The solubility limit of a-PHB in PLLAGA is around 20 wt % in both cases.

Chapter 3 Experimental

3.1 Material Used

The PLAs used in this work were commercially available products from NatureWorks LLC- an amorphous PLA (Grade 3251D) and a semi-crystalline PLA (Grade 7000D). The PLA (Grade 3251D) and the PLA (Grade 7000D) have the same density, reported as 1.24 g/cc. The PLA (Grade 3251D) has a reported M_n = 29,000 g/mol, M_w = 52,000 g/mol. The PLA (Grade 7000D) has a reported M_n = 80,000 g/mol, M_w = 150,000 g/mol. The copolyester EB062 used is a commercial polymer manufactured by Eastman Chemical Company, with a reported inherent viscosity about 0.75 dl/g. EB062 is essentially an amorphous copolyester material, with a crystallinity of less than 15% even after long periods under isothermal heating history.

3.2 Test samples preparation

3.2.1 Polymer blend I: low M.W. PLA (3251D) and EB062

A Werner &Phlerdever Corp. (2SK-30) self-wiping co-rotating twin-screw extruder was used to make the PLA/EB062 blends from pure PLA (3251D) and EB062 resin pellets. A uniform screw speed of 300 rpm was used for the extrusion. The blends prepared by melting blend at 220°C and 230°C, and they are summarized in Table 3-1and Table 3-2.

SAMPLE	PLA (wt %)	EB062 (wt %)	Operate Temp. (°C)
A1	100	-	220
A2	95	5	220
A3	90	10	220
A4	80	20	220
A5	50	50	220
A6	20	80	220
A7	10	90	220

Table 3-1 Sample designation and relevant sample components

SAMPLE	PLA (wt %)	EB062 (wt %)	Operate Temp. (°C)
B1	100	-	230
B2	95	5	230
B3	90	10	230
B4	80	20	230
B5	50	50	230
B6	20	80	230
B7	10	90	230

Table 3-2 Sample designation and relevant sample components

A nitrogen purge was used to protect material from oxidative degradation. Prior to extrusion, blend materials were overnight dried using an Aircon hopper/drier at 60°C and 67°C for PLA and EB062, respectively. The extrudate was pulled through a cool water bath and a pelletizer to obtain the blend pellets.

3.2.2 Polymer blend II: High M.W. PLA (7000D) and EB062

A Werner & Phleiderer Corp. (2SK-30) self-wiping co-rotating twin-screw extruder was used to make the PLA/EB062 blends from pure PLA (7000D) and EB062 resin pellets. A uniform screw speed of 300 rpm was used for the extrusion. The blends prepared by melting blend at 200°C and 220°C, and they are summered in Table 3-3 and Table 3-4.

SAMPLE	PLA(7000D) (wt %)	EB062 (wt %)	Operate Temp. (°C)
C1	100	-	200
C2	95	5	200
C3	90	10	200
C4	80	20	200
C5	50	50	200
C6	20	80	200
С7	10	90	200

Table 3-3 Sample designation and relevant sample components

Table 3-4 Sample designation and relevant sample components

SAMPLE	PLA(7000D) (wt %)	EB062 (wt %)	Operate Temp. (°C)
D1	100	-	220
D2	95	5	220
D3	90	10	220
D4	80	20	220
D5	50	50	220
D6	20	80	220
D7	10	90	220

A nitrogen purge was used to protect material from oxidative degradation. Prior to extrusion, blend materials were overnight dried using an Aircon hopper/drier at 58°C and 67°C for PLA and EB062, respectively. The extrudate was pulled through a cool water bath and a pelletizer to obtain the blend pellets.

3.3 Characterizations

Material characterization

The thermal characteristics of the virgin polymers and the blends prepared were measured using a Perkin Elmer differential scanning calorimetry (DSC-7) in unsealed aluminum pans in a dry nitrogen atmosphere with an empty aluminum pan as reference. All the data collected from the procedure of heating up the amorphous polymers after quenched from melting condition at cooling rate of 300°C/min. The melting behaviors of virgin polymers and blends made of low M.W. PLA (3251D) were monitored with differential scanning calorimetry at preset heating rates of 10°C/min, while the heating rate to measure the thermal properties of blends made of high M.W. PLA (7000D) was 1 °C/min. The melting points for each of the blends and the pure blend components were taken as the temperature of the endothermic peak maximum.

Rheological characterization

The rheological measurements were performed with a capillary rheometer (Instron Capillary Rheometer). The capillary was configured as follows: 1.008 inch for the length, 0.0304 inch for the diameter, and 0.375 inch for the barrel. The entrance pressure drop was determined instantaneously by an orifice (zero-length capillary) under the same respectively. The temperature of the barrel was set at 220°C, and the shear rate ranged from 10 to 10^4 s⁻¹. All the samples were dried at 60°C for 8 h. Before the tests, the samples were preheated for 5 minutes in two barrels.

Chapter 4 Results and discussion

4.1 Polymer blend I: Low M.W. PLA (3251D) and EB062

4.1.1 Melting behavior of neat PLA (3251D) and EB062

The crystallization and melting behaviors of the PLA (3251D) and EB062 are shown in Figure 4-1 and Figure 4-2. The glass transition temperature (taken as the middle point of the transition) of PLA (3251D) and EB062 are 60 °C and 82 °C respectively. The crystallization temperature of PLA (3251D) is 169 °C. There is no crystallization temperature for amorphous polymer EB062. The sharp peak on the shoulder of EB062 at 82 °C can be attributed to aging history.



Figure 4-1 DSC second heating thermograms for pure PLA (3251D)



Figure 4-2 DSC second heating thermograms for EB062
4.1.2 Melting behavior of PLA (3251D)/EB062 blends

4.1.2.1 Effect of different EB062 composition in the blend

The thermal properties of melt-quenched PLA/EB062 blends were evaluated by DSC from glassy state at a heating rate of 10° C min⁻¹. All the data are given in Table 4-1. T_g, T_c, and T_m represent glass transition, cold crystallization, and melting temperature, respectively. The X(PLA) is the weight fraction of PLA in the blend. The crystallinity (Xc) of crystallized films were calculated according to the following equations [29]:

Non-normalized Xc (DSC) (%) =100
$$\Delta$$
H (M)/ Δ H (M)⁰ (1)

Normalized Xc (DSC) (%) = Non-normalized Xc (DSC) (%) /
$$X_{PLA}$$
 (2)

where $\Delta H (M)^0$ is the enthalpy of melting of PLA crystal having an infinite thickness. We used the value of 93J/g reported by Fischer et al. as $\Delta H (M)^0$ [4].

SAMPLE ID	X ^a (PLA)	qa ^b (PLA)	Tg ^b (EB062)	T _c ^b	T _m b	ΔH(M) ^c	Non-normalized	normalized
	(wt %)	(°C)	(°C)	(°C)	(°C)	(J/g)	Xc (DSC) (%)	Xc (DSC) (%)
pure PLA	100	60	-	108	169	42	45	45
blend PLA/EB062	95	59	-	111	170	40	43	45
blend PLA/EB062	90	60	82	113	170	38	41	45
blend PLA/EB062	80	59	82	115	169	33	35	44
blend PLA/EB062	50	59	82	114	170	21	23	45
blend PLA/EB062	20	59	81	113	169	1	1	5
blend PLA/EB062	10	58	81	-	-	-	-	-
pure EB062	0	-	82	-	-	-	-	-

Table 4-1 Thermal properties of polymer blends made of PLA (3251D) at 220°C

^a $X(PLA) = W_{PLA}/W_{PLA} + W_{EB062}$, where W_{PLA} and W_{EB062} are weights of PLA and EB062, respectively.

 b T_g and T_m are glass transition and melting temperatures, respectively.

^c Enthalpy of melting.

The measurement of $T_g(s)$ is one of the conventional techniques to assess the miscibility (e.g., complete miscible, partially miscible and completely immiscible) of binary polymer blends. The blend is defined as miscible if it exhibits a single T_g while two distinct T_g 's are indicative of a two phase system (partially miscible or completely immiscible).

Table 4-1 shows some interesting features. First, when the percentage of PLA (3251D) is below 5 wt%, only one T_g shows up. This suggests the miscibility of the two blend components in the molten state. The two glass transition temperatures were observed for

the blend with PLA (wt%)>10 at temperatures around 59 °C and 82 °C, which are in agreement with the T_g values of pure PLA and EB062, respectively. These findings are indicative of the fact that PLA and EB062 are completely immiscible.



Figure 4-3 T_c of blend made of PLA (3251D) at 220°C

Second the EB062 affects crystallization of PLA. Figure 4-3 shows that, when PLA composition is above 80 wt%, the T_c values of the blends increased with decreasing of PLA (3251D) composition. This reveals that the very small amount of EB062 chains present in PLA-rich phase delayed the crystallization of PLA.

Third, the melting peaks are at a constant temperature around 170°C for the pure PLA and blends with various compositions of PLA above 10%. On the other hand, neither cold crystallization peak nor melting peak was observed for the blend with PLA composition below 10 wt%, revealing that they are not crystallizable.

Figure 4-4 shows the non-normalized crystallinity (Xc) of blend made of PLA (3251D) at 220°C. For Xc (DSC) values, we used the value of 93 J/g reported by Fischer et al. as Δ H (M) ⁰[39]. As seen in Figure 4-4, the Xc values increased linearly with increasing PLA content. Figure 4-5 shows the normalized Xc (DSC) of the blends. The normalized Xc (DSC) values were practically constant for PLA (wt%)>50. This indicates that the coexisting EB062 did not influence the normalized Xc of PLA for PLA content above 50 wt% after the completion of crystallization. On the other hand, the normalized Xc (DSC) values were practically small for PLA (wt%)<10, reflecting that PLA could not crystallize in the presence of a large amount of EB062. The large amount of EB062 surrounding PLA could have disturbed the formation of PLA crystallite nuclei or the growth of PLA crystallites in the limited crystallization period.



Figure 4-4 Non-normalized crystallinity (Xc) estimated by DSC measurements of blend

made of PLA (3251D) at 220°C



Figure 4-5 Normalized crystallinity (Xc) estimated by DSC measurements of blend made

of PLA (3251D) at 220° C

4.1.2.2 Effect of different extrusion temperature

The majority of polymer blends possess a multiphase morphology, and in most cases the satisfactory physical and mechanical properties of these materials are related to the presence of a stabilized finely dispersed phase. With a concern that low operation temperature leads to low efficiency to well mix the polymer blends, higher temperature was chosen. In Table 4-2 are the data collected from blends made of EB062 and PLA (3251D) at 230°C:

SAMPLE ID	X ^a (PLA) (wt %)	Tg ^b (PLA) (°C)	Tg ^b (EB062) (°C)	T _c ^b (°C)	T _m b (°C)	ΔH(M) ^c (J/g)	Non- normalized	normalized
							Xc (DSC) (%)	Xc (DSC) (%)
pure PLA	100	60	-	108	169	42	45	45
blend PLA/EB062	95	59	-	111	170	40	43	45
blend PLA/EB062	90	60	82	113	170	38	41	45
blend PLA/EB062	80	59	82	115	169	35	38	47
blend PLA/EB062	50	59	82	114	170	21	23	45
blend PLA/EB062	20	59	82	113	169	3	3	16
blend PLA/EB062	10	58	81	-	-	-	-	-
pure EB062	0	-	82	-	-	-	-	-

Table 4-2 Thermal properties of polymer blends made of PLA (3251D) at 230°C

^a $X(PLA) = W_{PLA}/W_{PLA}+W_{EB062}$, where W_{PLA} and W_{EB062} are weights of PLA and EB062,

respectively.

- b T_g and T_m are glass transition and melting temperatures, respectively.
- ^c Enthalpy of melting.

The binary polymer blends, when X_{PLA} (3251D) is below 5 wt%, likewise exhibited only one T_g , suggesting the miscibility of the two blend components in the molten state. The two glass transitions were observed for the blend with PLA (wt%)<95 at temperatures around 59 °C and 82 °C, showing that PLA and EB062 are immiscible. And the melting peaks are observed to be at a constant temperature of 170°C for the pure PLA and blends with PLA composition above 10 wt%. As seen in Figure 4-6, T_c is showing the same tendency as the results obtained from blend produced at 220°C. When PLA composition is above 80 wt%, T_c increases with the decrease of X_{PLA} (3251D) in the blend.



Figure 4-6 T_c of blend made of PLA (3251D) at 230°C

Figure 4-7 shows the Non-normalized crystallinity (Xc) of blend made of PLA (3251D) at 220°C increased linearly with increasing X_{PLA} (3251D). In Figure 4-8 the normalized Xc (DSC) values are practically constant for PLA (wt%)>50. The normalized Xc (DSC) values are practically zero for PLA (wt%)<10, reflecting that PLA could not crystallize in the presence of a large amount of EB062.



Figure 4-7 Non-normalized crystallinity (Xc) estimated by DSC measurements of blend

made of PLA (3251D) at 230°C





of PLA (3251D) at 230°C

A possible reason for the normalized Xc (DSC) values maintain constant value for PLA (wt%)>50, both for the blends produced at 220°C and 230°C, is that the coexisting EB062 did not influence the crystallization of the blend for PLA (wt%)>50. But when the large amount of EB062 surrounding PLA, they should have disturbed the formation of PLA crystallite nuclei or the growth of PLA crystallites in the limited crystallization period. In this way, PLA could not crystallize for PLA (wt %)< 10.

After compareing all the data given in Table 3 and Table 4, we find that most of the thermal properties of the blends are the same. This shows different operation temperatures 220°C and 230°C do not contribute too much to the improvement of the multiphase morphology and thus the final mechanical properties of these blends made with PLA(3251D).

4.1.2.3 Effect of different annealing time

In the next reheating test experiments, we hold the molten polymer blends at 220° C for 0, 10, 20, 45 and 120 minutes, with an anticipation that a longer holding time while the polymer is in the molten state will increase the possibility of transesterification to occur between the two components. Each time we quench the sample back to 30° C at a cooling rate 300° C/min before reheating it to the melt.

From Figure 4-9 to Figure 4-14 illustrate the DSC heating thermograms of blends made of PLA (3251D) that had been annealed at 220 °C for different times. From these DSC thermograms of blends made of PLA (3251D) at 220 °C, which are shown below, we can find out that the T_g of PLA and EB062, if available, are constant irrespective of the annealing time. In the blends, the crystallization temperatures T_c and melting temperature T_m of PLA are, in fact, depend not only on the blend composition and also on the annealing time. The crystal peaks and melting peaks of the blend exist when PLA content is higher than 10 wt%. For PLA content of 50% in the blend, the T_c increases with the increasing annealing time, whereas it increases more evidently when PLA content in the blend is 95%. Meanwhile, an increase in the annealing time results in the decline of T_m. There is no crystallization when PLA (wt %)< 10.



Figure 4-9 Heat flow rate vs. temperature of PLA/EB062 95/5 blends (220°C) heating at 10°C/min after cooling from the melt at 300°C/min.

clarity.



Figure 4-10 Heat flow rate vs. temperature of PLA/EB062 90/10 blends (220°C) heating at 10°C/min after cooling from the melt at 300°C/min.



Figure 4-11 Heat flow rate vs. temperature of PLA/EB062 80/20 blends (220°C) heating at 10°C/min after cooling from the melt at 300°C/min.



Figure 4-12 Heat flow rate vs. temperature of PLA/EB062 50/50 blends (220°C) heating at 10°C/min after cooling from the melt at 300°C/min.



Figure 4-13 Heat flow rate vs. temperature of PLA/EB062 20/80 blends (220°C) heating at 10°C/min after cooling from the melt at 300°C/min.



Figure 4-14 Heat flow rate vs. temperature of PLA/EB062 10/90 blends (220°C) heating at 10°C/min after cooling from the melt at 300°C/min.

4.2 Polymer blend II: High M.W. PLA (7000D) and EB062

4.2.1 Why change PLA?

Polymer blends which possess a multiphase morphology, the control of the morphology of the dispersed phase in such systems depends on varying degrees of interfacial interaction [40], viscosity ratio [40], shear rate [45], elasticity of components [46], and processing conditions [42]. The particle size of the dispersed phase and its dependence on the parameters described above is given by:

$$a = \frac{4\gamma}{G\eta_m} \left(\frac{\eta_d}{\eta_m}\right)^{0.84}$$

Equation 3 dispersed phase particle size equation [40]

G is the rate of mixing, γ is the interfacial tension, η_m and η_d are the melt viscosities of the matrix and the dispersed phases respectively. Specifically in this research, η_m and η_d represent the viscosity of PLA and EB062, respectively. By choosing a higher molecular weight PLA, the melt viscosities of the two blend components become closer to each other and thus potentially reducing the values of $-a^{"}$. In Figure 4-15 are the apparent viscosities of PLA 3251D, PLA 7000D, and EB062. And it is showing that the melting viscosity of high molecular weight of PLA is closer to that of EB062.



Figure 4-15 Apparent viscosity of PLA 3251D, PLA 7000D, and EB062

4.2.2 Melting behavior of neat PLA (7000D) and EB062

The crystallization and melting behaviors of the PLA (7000D) and PLA (3251D) are like each other. The glass transition temperature (taken as the middle point of the transition) of neat PLA (7000D) and EB062 are 56°C and 82°C, respectively. The crystallization temperature and melting temperature of neat PLA (7000D) are 122°C and 156°C.

4.2.3 Melting behavior of blend made of PLA (7000D) and EB062

4.2.3.1 Effect of different EB062 composition in the blend

In Table 4-3 are the data collected from blends made of EB062 and PLA (7000D) at 220° C. Some similar features have been observed for the blend made of PLA (7000D). The two glass transitions were observed for the blends with PLA (wt %)< 50, at temperatures around 56 °C and 78 °C. The value 56 °C is in agreement with the T_g value of pure PLA, but the other measured value 78 °C is below the T_g of pure EB062, which is 82 °C. These findings are indicative of the fact that PLA and EB062 are possible partly miscible. When only one T_g shows up, the percentage of PLA (7000D) involved in the binary blend increases from 5wt% to 20 wt%. This suggests the miscibility of the two

blend components in the molten state is related with viscosity of PLA. The melting peaks are observed at a constant temperature around 157 °C for blends with PLA composition above 50 wt%.

	X ^a (PLA) (wt %)	Tg ^b (PLA) (°C)	Tg ^b (EB062) (°C)	T _c ^b (°C)	T _m ^b	ΔH(M) ^c (J/g)	Non- normalized	normalized
SAMPLE ID					(°C)		Xc (DSC) (%)	Xc (DSC) (%)
pure PLA	100	57	-	113	158	28	30	30
blend PLA/EB062	95	57	-	111	157	27	29	31
blend PLA/EB062	90	57	-	111	157	24	26	29
blend PLA/EB062	80	56	-	114	157	21	23	28
blend PLA/EB062	50	56	79	112	158	14	15	30
blend PLA/EB062	20	56	78	-	-	-	-	-
blend PLA/EB062	10	55	78	-	-	-	-	-
pure EB062	0	-	82	-	-	-	-	-

Table 4-3 Thermal properties of polymer blends made of PLA (7000D) at 220°C

^a $X(PLA) = W_{PLA}/W_{PLA}+W_{EB062}$, where W_{PLA} and W_{EB062} are weights of PLA and EB062, respectively.

 $^{b}~~T_{g}$ and T_{m} are glass transition and melting temperatures, respectively.

^c Enthalpy of melting.

Figure 4-16 shows the T_c values of the blends first decreased and then increased with decreasing of PLA (7000D) composition. This reveals that the very small amount of EB062 chains present in PLA-rich phase delayed the crystallization of PLA. But this delay crystallization effect becomes weaker with the increasing EB062 composition in the blend. No cold crystallization peak is observed for the blends with PLA composition below 50 wt% revealing that they are not crystallizable.



Figure 4-16 T_c of blend made of PLA (7000D) at 220°C

Figure 4-17 shows the non-normalized crystallinity (Xc) of blends made of PLA (7000D) at 220°C. The X(PLA) is the weight fraction of PLA in the blend. The crystallinity (Xc) of crystallized films were calculated according to the following equations [29]:

Non-normalized Xc (DSC) (%) =100
$$\Delta$$
H (M)/ Δ H (M)⁰ (4)

Normalized Xc (DSC) (%) = Non-normalized Xc (DSC) (%) /
$$X_{PLA}$$
 (5)

Here $\Delta H (M)^0$ is the enthalpy of melting of PLA crystal having an infinite thickness. We used the value of 93J/g reported by Fischer et al. as $\Delta H (M)^0$ [4].

As seen in Figure 4-17, the Xc values increase linearly with increasing PLA (wt%). Figure 4-18 shows the normalized Xc (DSC) of the blends. The normalized Xc (DSC) values for PLA (wt %)> 50 were practically constant around 30. It is higher than the normalized Xc (DSC) value of neat PLA. That is because the neat PLA did not go through the extrusion process. The normalized Xc (DSC) values is practically zero for PLA (wt%)<20.



Figure 4-17 Non-normalized crystallinity (Xc) estimated by DSC measurements of blend made of PLA (7000D) at 220°C



Figure 4-18 Normalized crystallinity (Xc) estimated by DSC measurements of blend made of PLA (7000D) at 220°C

4.2.3.2 Effect of different extrusion temperature

In Table 4-4 are the data collected from blends made of EB062 and PLA (7000D) at 200°C. Compare the data of polymer blends processed at 220 °C and 200 °C, when only one T_g shows up, the PLA (7000D) content in the blends drops from 20 wt% to 5wt%. Two glass transitions are observed for the blend with PLA (wt %)<95, indicating the components of the blend are immiscible. It also shows the different operation temperatures do not have much effect on the transesterification occurring between the two components.

SAMPLE ID	X ^a (PLA) (wt %)	Tg ^b (PLA) (°C)	Tg ^b (EB062) (°C)	T _c ^b (°C)	T _m b	ΔH(M) ^c (J/g)	Non- normalized	Normalized
					(°C)		Xc (DSC) (%)	Xc (DSC) (%)
pure PLA	100	57	-	112	158	28	30	30
blend PLA/EB062	95	56	-	109	157	24	26	27
blend PLA/EB062	90	56	79	108	157	22	24	26
blend PLA/EB062	80	57	80	111	157	18	19	24
blend PLA/EB062	50	56	78	112	158	13	14	28
blend PLA/EB062	20	56	78	-	-	-	-	-
blend PLA/EB062	10	56	79	-	-	-	-	-
pure EB062	0	-	82	-	-	-	-	-

Table 4-4 Thermal properties of polymer blends made of PLA (7000D) at 200°C

^a $X(PLA) = W_{PLA}/W_{PLA} + W_{EB062}$, where W_{PLA} and W_{EB062} are weights of PLA and EB062,

respectively.

 $^{\rm b}~T_{\rm g}$ and $T_{\rm m}$ are glass transition and melting temperatures, respectively.

^c Enthalpy of melting.

Figure 4-19 shows the T_c values of the blends made of PLA 7000D likewise first decreases then increase with the decreasing of PLA (7000D) composition. Figure 4-20 depicts the Xc values increased linearly with increasing PLA (wt %). On Figure 4-21 the normalized Xc (DSC) values were around 27% for PLA (wt%)>50, which is lower than the value (30%) get from blends processed at 220°C. One possible explanation is that the blends produced at higher temperature went through more thermal degradation than the blends made at lower temperature. Thermal degradation lowers the IV value of PLA and thus leads to high crystallinity. Meanwhile, the normalized Xc (DSC) values were practically zero for PLA (wt%)<50.



Figure 4-19 T_c of blend made of PLA (7000D) at 200°C



Figure 4-20 Non-normalized crystallinity (Xc) estimated by DSC measurements of blend

made of PLA (7000D) at 200°C



Figure 4-21 Normalized crystallinity (Xc) estimated by DSC measurements of blend made of PLA (7000D) at 200°C

4.2.3.3 Effect of different annealing time

Figure 4-22 to Figure 4-27 illustrate the DSC heating thermograms of the 1°C/min meltcooled samples that had been annealed at 220 °C for different times. From these figures, we can conclude that the T_g of PLA and EB062, if present, are constant value regarding to different annealing time. When PLA (wt%)>20, The T_c of the blends shift to higher value while the T_m of the blends shift to lower one with the longer annealing time. There is no crystallization when PLA content in the blend is lower than 20 wt%.



Figure 4-22 Heat flow rate vs. temperature of PLA/EB062 95/5 blends (220°C) heating at 1°C/min after cooling from the melt at 300°C/min.



Figure 4-23 Heat flow rate vs. temperature of PLA/EB062 90/10 blends (220°C) heating 1°C/min after cooling from the melt at 300°C/min.



Figure 4-24 Heat flow rate vs. temperature of PLA/EB062 80/20 blends (220°C) heating 1°C/min after cooling from the melt at 300°C/min.



Figure 4-25 Heat flow rate vs. temperature of PLA/EB062 50/50 blends (220°C) heating 1°C/min after cooling from the melt at 300°C/min.



Figure 4-26 Heat flow rate vs. temperature of PLA/EB062 20/80 blends (220°C) heating 1°C/min after cooling from the melt at 300°C/min.



Figure 4-27 Heat flow rate vs. temperature of PLA/EB062 10/90 blends (220°C) heating 1°C/min after cooling from the melt at 300°C/min.

There is a concern that all the features observed from the annealing test are due to one of the two components in the blends. To have a better understanding about the T_c and T_m shifting, we do the same annealing test for the neat PLA 3251D and PLA 7000D.

Figure 4-28 and Figure 4-29 are thermographs of neat PLA 3251D and PLA 7000D undergoing the annealing test. The same features are observed again. The T_c of the blends shift to higher value while the T_m of the blends shift to low value with the longer annealing time. Based on this, we can conclude all the thermal property changes seen previously are mainly due to the pure PLA thermal properties changes.


Figure 4-28 Heat flow rate vs. temperature of pure PLA (3251D) heating at 10° C/min after cooling from the melt at 300° C/min



Figure 4-29 Heat flow rate vs. temperature of pure PLA (7000D) heating at 10°C/min after cooling from the melt at 300°C/min

4.3 Polylactide Copolymers

Poly (lactide) (PLA) has stereoisomers, such as poly (L-lactide) (PLLA), poly (D-lactide) (PDLA), and poly (DL-lactide) (PDLLA). Isotactic and optically active PLLA and PDLA are crystalline, whereas relatively atactic and optically inactive PDLLA is amorphous [47]. The mechanical properties and crystallization behavior of PLA are very dependent on the molecular weight and stereochemical makeup of the backbone. The stereochemical makeup is very easily controlled by the polymerization with D- lactide, L-lactide, D, Llactide, or meso-lactide, to form random or block stereocopolymers [48]. Pure poly(Dlactide) or poly (L-lactide) has an equilibrium crystalline melting point of 207°C [50], but typical melting points are in the 170-180oC range. This is due to small and imperfect crystallites, slight racemization, and impurities. Perego et al. [51] studied the effects of molecular weight and crystallinity on the mechanical properties of PLA by polymerizing pure L-lactide and D, L-lactide to create amorphous or semicrystalline polymers. They found that the glass transition temperature wasn't greatly affected by the stereochemical makeup or the range of molecular weights tested. Bigg [52] had shown table of the various PLA samples investigated. The primary transition temperatures and melting temperatures of PLA copolymers are present in Table 4-5. The primary transition temperatures and melting temperatures of PLA copolymers are presented in Table 4-5.

Copolymer ratio	Glass transition temp. (°C)	Melting Temperature, (°C)
100/0 (L/D,L)-PLA	63	178
95/5 (l/d,l)-PLA	59	164
90/10 (l/d,l)-PLA	56	150
85/15 (l/d,l)-PLA	56	140
80/20 (l/d,l)-PLA	56	(125) ^a

Table 4-5 Primary Transition Temperatures of Selected PLA Copolymers [52]

^aMelting point achieved by strain crystallization

After comparing the melting temperatures of PLA copolymers with different copolymer ratios, we can conclude that the more D, L-lactide involved in the PLA copolymer, the lower melting temperatures are.

Leevameng Bouapao et al. [54] investigated the effect of incorporated PDLLA on the PLLA/PDLLA blends at different blending ratio. The two glass transitions were observed for the blend films, when the PLLA composition involved in the blend between 0.3 and 0.9. The two temperatures are at constant temperatures around 50 and 60 $^{\circ}$ C, which are in agreement with the T_g values of pure PDLLA and PLLA films, respectively. These findings are indicating that PLLA and PDLLA are immiscible with each other. However, Zhang J [56], Ren J [57], and Chen CC [58] believed the PLLA/PDLLA blends are miscible with each other, because of the observation of a single T_g in the PLLA/L-lactide-rich PLA blends.

Leevameng Bouapao et al. [54] also found that the T_c values of the blend films increased with the deceasing PLLA content, shown in Figure 4-30.



Figure 4-30 DSC thermograms of pure PLLA, PDLLA, and blend films crystallized isothermally at Tc of 130°C for 10 h (a) and their magnified glass transition peaks [54].

This reveals that PDLLA chains present in the PLLA-rich phase delayed the crystallization of PLLA. However, the melting peaks were observed at a constant temperature for the blend films with PLLA content above 0.3. This is a very similar to my results observed in the annealing test experiments.

H. Inata and S. Matsumura studied the poly (L-lactide-co-meso-lactide) blend, and concluded that the blending of crystalline PLLA or PDLA with amorphous PDLLA is effective for controlling the overall crystallinity (Xc). The crystallization of PLLA takes place when the PLLA content higher than 0.2 and spherulites are formed at the PLLA content exceeding 0.6 [59]. Leevameng Bouapao et al. [52] also analyzed the blends of crystalline and amorphous poly (lactide)s. Their non-isothermal crystallization analysis is shown in Figure 4-31.



Figure 4-31 non-normalized crystallinity estimated by DSC and X-ray diffractometry of pure PLLA and blend films crystallized isothermally at T_c of 130°C for 10 h [54].

The non-normalized crystallinity increased linearly with increasing the composition of PLLA involved in the blends. In our research, we also get the same relationship between the non-normalized crystallinity and composition of PLA's. In Leevameng's experiment, the normalized crystallinity of blend films were practically constant for $X_{PLLA} = 0.3-1$, shown below in Figure 4-32.



Figure 4-32 Normalized crystallinity of pure PLLA and blend films crystallized isothermally at T_c of 130°C for 10h [54].

This result is in agreement with the research conclusion got by Tsuji H, Ikada and A. C. Ibay [59]. On the other hand, as seen in Figure 4-32, the normalized Xc (DSC) value was practically zero for $X_{PLLA} = 0.1$, reflecting that the large amount of PDLLA surrounding

PLLA didn't disturbe the formation of PLLA crystallite nuclei or the growth of PLLA. In our results, we also get the similar relation between normalized crystallinity and PLA composition involved. The only difference is that a decreasing tendency appears when only little PLA (20 wt %) involved in our blends.

Based on above analysis, we found out that there is big similarity between the blends made of PLLA and PDLLA and our blend samples made of PLA copolymer and polyester:

- In the presence of PDLLA or polyester (EB062), PLLA or PLA copolymer could crystallize and form the spherulites or crystalline assemblies for the X_{PLLA} or X_{PLA} above certain value.
- [2] The crystallization temperature will vary with either X_{PLLA} or different annealing time at high temperature. However, the melting temperatures approximately keep constant.
- [3] The crystallinity will keep constant, irrespective of either X_{PLLA} or different annealing time at high temperature.

Recently, Tsukegi et al. reported that at temperature less than 200°C, conversion of PLLA into meso-lactide and oligomers was minimal. However, above this temperature, the formation of meso-lactide became quite significant (4.5 wt% at 200 °C and 38.7 wt% at 300 °C for 120 min heating). According to above analyzes, a probable reason could present to explain all the features we have been found during the annealing tests. When blends made of PLA copolymer and polyester (EB062) exposed to elevated temperatures for long time, the PLLA involved in the PLA copolymer probably would undergo

racemization to form meso-lactide, and therefore impact the material properties of the resulting PLA polymer.

Chapter 5 Conclusions and recommendation

5.1 Recommendations

This thesis presents the effect of the composition and operation conditions on the properties of immiscible PLA/EB062 blends obtained by reactive extrusion. In our research, for low M.W. polymer PLA (3251D), the two blend components in the molten state are miscible with each other only when the composition of PLA (3251D) is below 5 wt% and different operation temperatures do not help to improve this situation. For PLA (7000D) blends operated at 220°C, even when the percentage of PLA (7000D) from 5 wt% to 20 wt%, there is still only one T_g.

Small amount of EB062 chains in the PLA-rich phase could increase the T_c values, for both blends made with PLA (3251D) and PLA (7000D). However, the melting peaks for the blends are irrelative with the composition of EB062 involved in. This indicates the incorporated EB062 has little effect on the final crystalline levels of PLA.

The normalized crystallinity (Xc) of blends made of PLA (3251D), either at 220°C or 230°C, are practically constant for PLA content above 50 wt%, indicating the coexisting EB062 does not influence the crystallization of the blend. And the normalized Xc (DSC) values were practically zero for PLA (wt%) = 10, reflecting that PLA could not crystallize in the presence of a large amount of EB062. Meanwhile, the blends made of

PLA (7000D) showed the same tendency. The normalized crystallinity (Xc) of blend made of PLA (7000D), irrespective of the operation temperature, are practically constant for X_{PLA} =50 wt%- 90 wt%. When X_{PLA} <20 wt%, the normalized Xc (DSC) values are practically zero. However, the measured value Xc of the blend with X_{PLA} = 90 wt% is higher than the Xc of the pure PLA (7000D).

The crystal temperature, the melting temperature and crystallinity of blend will vary with the increasing annealing time at 220°C. The larger PLA's composition in the blend is, the more obvious the T_c and T_m shifting shows. And the same features are observed when the pure PLA (both 3251D and 7000D) under annealing test. Based on this, we conclude that the shifting of T_c and T_m of the blend are mainly due to the PLA component changes.

5.2 Recommendations

The effects of many important factors such as temperature, time, blend composition and initial IV of the precursor were investigated. A comprehensive investigation of the transesterification reaction of PLA/EB062 blends should also include the study of other factors such as the different PLA sources (homopolymers, copolymers and branched polymer) and the catalyst systems used in preparation of the PLA and PET blends.

All the PLA/EB062 blends discussed above were produced at constant screw rotation speed at 300rpm. In general, a higher rotor speed leads to a higher shearing in the extruder. This increased shearing promotes a better dispersive mixing of the blend

components, with a reduction in particle size of the dispersed phase. However, high rotation speed will limited the residual time of the components in the extruder. The short residual time may affect the transesterification between the two components. If possible, the future job should be done at low rotation speed.

References

[1] Sodergard, A. Scolt, M., –Properties of Lactic Acid Based Polymers and Their Correlation with Compositions," Progress in Polymer Science 2002, vol. 27, 1123-1163.

[2] Van de Velde, K.; Kiekens, P., –Biopolymers: overview of several properties and consequences on their applications," Polymer Testing 2002, vol. 21, 433-442.

[3] Lunt J, —Large-scale production, properties and commercial applications of polylactic acid polymers," Polymer Degradation and Stability 1998, vol. 59, 145–152

[4] Miyata, T. and T. Masuko, -Crystallization behaviour of poly(L-lactide)," Polymer 1998, vol. 39, 5515-5521.

[5] Iannace S, Maffezzoli A, Leo G., –Influence of crystal and amorphous phase morphology on hydrolytic degradation of PLLA subjected to different processing conditions," Polymer April 2001, vol. 42, no. 8, 3799-3807.

[6] Wehrenberg R. H., II, -Lactic acid polymers: strong, degradable thermoplastics," Materials Engineering 1981, vol. 93, no. 3, 63.

[7] Lipinsky, E.S., Sinclair, R.G., -Is lactic acid a commodity chemical?" Chemical Engineering Progress 1986, vol. 82, no. 8, 26-32.

[8] Garlotta D., –A literature review of poly(lactic acid)," Journal of Polymers and the Environment 2001, vol. 9, no. 2, 63-84.

[9] Datta R. Henry M., -Lactic acid: recent advances in products. processes and

[10] technologies-a review," Journal of Chemical Technology and Biotechnology 2006, vol. 81, 1119-1129.

[11] Jamshidi K, Hyon S-.H, and Ikada Y, —Thermal characterization of polylactides," Polymer 1988, vol. 29, 2229–2234.

[12] Spinu M., Jackson C., Keating M.Y. and Gardner K.H., –Material design in poly(lactic acid) systems: block copolymers, star homo- and copolymers, and stereocomplexes," Journal of Macromolecular Science, Part A: Pure and Applied Chemistry, 1520-5738, vol. 33, Issue 10, 1996, 1497 – 1530.

[13] Safa H.L. and Bourelle F., -Sorption-desorption of aromas on multi-use PET bottles—a test procedure," Packaging Technology and Science 1999, vol. 12, no. 1, 37–44.

[14] Parikh K., Cattanach K., Rao R., Suh D.S., Wu A.M., Manohar S.K., –Flexible vapour sensors using single walled carbon nanotubes," Sensor and Actuators 2006, B 113, 55-63.

[15] Wu M., Shaw L.L., –A novel concept of carbon-filled polymer blends for applications in PEM fuel cell bipolar plates," International Journal of Hydrogen Energy 2005, vol. 30, 373-380.

[16] Wu M., Shaw L.L., -On the improved properties of injectionmolded, carbon nanotube-filled PET/PVDF blends," Journal of Power Sources 2004, vol. 136, 37-44.

[17] Papadopoulou C. P., Kalfoglou N. K., -Compatibility behaviour of blends of poly(ethylene terephthalate) with an amorphous copolyester," Polymer 1997, vol. 38, Issue 3, 631-637.

[18] EUROPEAN PATENT APPLICATION

[19] Baker W, Scott C. Hu GH., –Reactive polymer blending," Connecticut: Hanser.[20] 2001.

[21] Li, H. X., G. H. Hu, and J. A. Sousa, __The Early Stage of the Morphology Development of Immiscible Polymer Blends During Melt Blending: Compatibilized vs. Uncompatibilized Blends," Journal of Polymer Science: Part B: Polymer Physicas 1999, vol. 37, 3368.

[22] Stewart M. E., Cox A. J., Taylor D. M., –Reactive processing of poly(ethylene 2,6naphthalene dicarboxylate)/poly(ethylene terephthalate) blends," Polymer 1993, vol. 34, 4060-4067.

[23] Callander D. D., -Chapter 9 in Modern Polyesters: Chemistry and Technology of Polyesters and Copolymers," edited by J. Scheirs and T. E. Long, John Wiley & Sons, Ltd., 2003.

[24] Gupta V. B. and Bashir Z., -Chapter 7 in Handbook of Thermoplastic Polyesters," Vol.1, edited by Stoyko Fakirov, WILEY-VCH Verlag GmbH, Weinheim, 2002.

[25] Jabarin S. A., -A Course on PET Technology," The University of Toledo, 2003.

[26] Jabarin S. A. and Chandran P., –Biaxial orientation of Poly(ethylene terephthalate).Part III. Comparative structure and property changes resulting from simultaneous and sequential orientation," Advances in Polymer Technology 1993, Vol. 12, no. 2, 119.

[27] Jabarin S. A., –Orientation studies of poly(ethylene terephthalate)" Polymer Engineering and Science 1984,vol. 24, no.5, 376-384.

[28] Ohkoshi I, Abe H, Doi Y. –Miscibility and solid-state structures for blends of poly ((S)-lactide) with atactic poly ((R, S)-3-hydroxybutyrate)," Polymer 2000, vol. 41, 5985

- 5992.

[29] Koyama N, Doi Y. –Miscibility of binary blends of poly [(R) - 3-hydroxybutyric acid] and poly [(S)-lactic acid]," Polymer 1997, vol. 38, 1589 – 1593.

[30] Suyatma NE, Copinet A, Tighzert L, Coma V. –Mechanical and barrier properties of biodegradable films made from chitosan and poly(lactic acid) blend," Journal of Polymer and Environment 2004, vol. 12, no. 1, 1 – 6.

[31] Ke T, Sun X. –Effect of moisture content and heat treatment on the physical properties of starch and poly(lactic acid) blends," Journal of Applied Polymer Science 2001, vol. 81, 3069 – 3082.

[32] Khurma J R, Rohindra D R and Devi R, –Miscibility study of solution cast blends of poly(lactic acid) and poly(vinyl butyral)," The South Pacific Journal of Natural Science 2005, vol. 23, no. 1, 22 – 25.

[33] Hu Y., Hu Y.S., Topolkaraev V., Hiltner A., Baer E., -Crystallization and phase separation in blends of high stereoregular poly(lactide) with poly(ethylene glycol)," Polymer 2003, vol. 44, 5681–5689.

[34] Zhao P, Liu WQ, Wu QS, and Ren J, –Preparation, Mechanical, and Thermal properties of Biodegradable Polyesters/ Poly(Lactic Acid) Blends," Journal of Nanomaterials 2010, Article ID 287082, 8 pages.

[35] Yokohara T. and Yamaguchi M, -Structure and Properties for biomass-based polyester blends of PLA and PBS," European Polymer Journal March 2008, vol. 44, no. 3, 677-685.

[36] Bhatia A, Gupta R. K, Bhattacharya S. N. and Choi H. J., -Compatibility of biodegradable poly (lactic acid) (PLA) and poly (butylene succinate)(PBS) blends for

packaging application," Korea-Australia Rheology Journal November 2007, vol. 19, no. 3, 125-131.

[37] Mohamed A, Gordon S. H, Biresaw G, –Poly(lactic acid)/Polystyrene Bioblends Characterized by Thermogravimetric Analysis, Differential Scanning Calorimetry, and Photoacoustic Infrared Spectroscopy," Journal of Applied Polymer Science July 2007, vol. 106, no. 3, 1689-1696.

[38] Hu GH, Cartier H, Plummer C., -Reactive Extrusion: Toward Nanoblends," Macromolecules 1999, vol. 32, no. 14, 4713-4718.

[39] Fischer EW, Sterzel HG, Wegner G, Kolloid ZZ., –Investigation of the structure of solution grown crystals of lactide copolymers by means of chemical reactions," Polymer 1973, vol. 251, no. 11, 980-990.

[40] Wu, S., –Formation of dispersed phase in incompatible polymer blends: Interfacial and rheological effects," Polymer Engineering and Science March 1987, vol. 27, no. 5, 335-343.

[41] Willis, J. M.; Favis, B. D., *P*rocessing-morphology relationships of compatibilized polyolefin/polyamide blends. Part I: The effect of an lonomer compatibilizer on blend morphology," Polymer Engineering and Science November 1988, vol. 28, no. 21, 1416-1426.

[42] Favis, B. D.; Willis, J. M., –Phase size/composition dependence in immiscible blends: Experimental and theoretical considerations," Journal of Polymer Science Part B: Polymer Physics November 1990, vol. 28, no. 12, 2259–2269.

[43] Karger-Kocsis, J.; Kallo, A.; Kuleznev, N., –Phase structure of impact-modified polypropylene blends," Polymer February 1984, vol. 25, no. 2, 279-286.

78

[44] Favis, B. D.; Chalifoux, —The effect of viscosity ratio on the morphology of polypropylene/polycarbonate blends during processing," Polymer Engineering & Science November 1987, vol. 27, no. 21, 1591–1600.

[45] Min, K.; White, J. L.; Fellers, –High density polyethylene/polystyrene blends: Phase distribution morphology, rheological measurements, extrusion, and melt spinning behavior," Journal of Applied Polymer Science June 1984, vol. 29, no. 6, 2117–2142.

[46] Vanoene, H., -Modes of dispersion of viscoelastic fluids in flow," Journal of Colloid and Interface Science September 1972, vol. 40, no. 3, 448-467.

[47] Parag, G. G., Uttandaraman, S., –Prediction of dispersed phase drop diameter in polymer blends: The effect of elasticity," Polymer Engineering & Science June 1996, vol. 36, no. 12, 1656–1665.

[48] Bousmina, M., Alt-Kadi, A., Faisant, J. B., –Determination of shear rate and viscosity from batch mixer data," Journal of Rheology 1999, vol. 43, no. 2, 415-433.

[49] De Santis P, Kovacs A., -Molecular conformation of poly(S-lactic acid)," Biopolymers March 1968, vol. 6, no. 3, 299–306.

[50] Hartmann M. H, –Biopolymers from renewable resources," Springer, Berlin, Germany 1998, 367–411.

[51] Gilding D. K, Reed A. M, -Biodegradable Polymers for Use in Surgery-Poly(glycolic)/Poly(lactic acid) Homo-and Copolymers: 1," Polymer 1979, vol. 20, 1459-1464.

[52] Kricheldorf H. R, Kreiser-Saunders I, and Boettcher C, –Polylactones: 31. Sn(II)octoate-initiated polymerization of L-lactide: a mechanistic study," Polymer 1995, vol. 36, no. 6, 1253–1259.

79

[53] Perego G, Cella G. D, and Bastioli C, –Effect of molecular weight and crystallinity on poly(lactic acid) mechanical properties," Journal of Applied Polymer Science January 1996, vol. 59, 37–43.

[54] Bigg D. M, –Annual Technical Conference – Society of Plastics Engineers", 1996, 2028–2039.

[55] Leevameng Bouapao , Hideto Tsuji, -Crystallization, spherulite growth, and structure of blends of crystalline and amorphous poly(lactide)s," Polymer July 2009, vol. 50, no. 16, 4007-4017.

[56] Zhang J, Tashiro K, Tsuji H, Domb AJ., –Investigation of Phase Transitional Behavior of Poly(l-lactide)/Poly(d-lactide) Blend Used to Prepare the Highly-Oriented Stereocomplex," Macromolecules 2007, vol. 40, no. 4, 1049-1054.

[57] Ren J, Adachi K., –Dielectric Relaxation in Blends of Amorphous Poly(dl-lactic acid) and Semicrystalline Poly(l-lactic acid)," Macromolecules 2003, vol. 36, no. 14, 5180-5186.

[58] Chen CC, Chueh JY, Tseng H, Huang HM, Lee SY., –Preparation and characterization of biodegradable PLA polymeric blends," Biomaterials March 2003, vol. 24, no. 7, 1167-1173.

[59] Tsuji H, Ikada Y., –Blends of isotactic and atactic poly(lactide). I. Effects of mixing ratio of isomers on crystallization of blends from melt," Journal of Applied Polymer Science December 1995, vol. 58, no. 10, 1793–1802.

[60] Tsuji H, Ikada Y., –Blends of isotactic and atactic poly(lactide)s: 2. Molecularweight effects of atactic component on crystallization and morphology of equimolar blends from the melt," Polymer 1996, vol. 37, no. 4, 595-602.

80

[61] Tsuji H, Ikada Y., –Blends of crystalline and amorphous poly(lactide). III. Hydrolysis of solution-cast blend films," Journal of Applied Polymer Science February 1997, vol. 63, no. 7, 855–863.