Improvement of Mechanical and Thermal Properties
of Poly(lactic acid) with Polymer Blends

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Chapter 1

General Introduction

1.1 Biodegradable Polymers

Plastics have been widely used in various fields of applications for industries due to their low price, light weight and excellent properties. Because of these profits, a huge amount of plastics, which mostly made from fossil resources have been produced every year. As a result, the end-used plastic wastes generate severe environmental problems and a generation of large quantity of carbon dioxide has been promoting the global warming. Furthermore, the future limitation of petroleum source available for production of synthetic polymers must be taken into consideration. One way to solve these problems is replacing the commodity synthetic polymers with biobased and biodegradable polymers, which are friendly to environments and can be produced from renewable natural resources such as sugar and starch.\textsuperscript{1–3} The biodegradable polymers have received significant research interest as suitable replacements of non-degraded petroleum-based polymers. They have the ability to completely degrade in the presence of microorganisms.\textsuperscript{4}

Food packaging is one of the most utilization polymer materials produced from petroleum-based synthetic polymers. The packaging intends to have a rather short life cycle from food protection to rubbish. Therefore, most of the post-consumer plastic wastes come from food packaging. The application of biobased and biodegradable materials have been studied as alternatives to fossil-based polymers and proved to be a possible solution to reduce the
environmental pollution. This has accelerated the development of biodegradable polymers for plastic industry applications which comprises of (1) naturally occurring polymers, such as cellulose, starch, chitin, polyhydroxyalkanoates and poly(3-hydroxybutyrate), and (2) synthetic polymers, such as poly(lactic acid) (PLA), poly(butylene succinate) (PBS), poly[(butylene succinate)-co-adipate] (PBSA), and poly(ε-caprolactone) (PCL). Among these biodegradable polymers, PLA has received more attention from its degradability potential as well as excellent properties for industrial applications and the polymer can be derived from renewable resources.

Biodegradable polymers can be classified in four categories depending on their synthesis processes and sources of monomers as follows:

(a) Biodegradable polymers synthesized from biobased raw materials which can be classified to (1) polysaccharides, e.g., starches (wheat, potatoes, maize),13–15 lignocellulosic products (wood, straws, etc.)16 and others (pectins, chitin, chitosan, gums),17 and (2) protein and lipids, e.g., animals (casein, whey, collagen/gelatin),18–29 and plants (zein, soya and gluten),30,31

(b) Biodegradable polymers obtained by microbial production of biomass, e.g., polyhydroxyalkanoates (PHA) such as poly(hydroxybutyrate) (PHB) and poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV),

(c) Biodegradable polymers obtained by chemically synthesized process using monomers obtained from agro-resources, e.g., PLA, PBS, PBSA, etc.,

(d) Polymers whose monomers and polymers are both obtained by chemical synthesis from fossil resources such as PCL, polyesteramides (PEA), aliphatic copolysters (PBSA) and aromatic co-polyesters (PBAT).32

Synthetic polymers are gradually being replaced by biodegradable materials.
especially those derived from natural resources. Recent innovations in edible and/or biodegradable polymer films have been widely reported,\textsuperscript{12,33–36} presenting improvements in food packaging and medical applications.

1.2 Poly(lactic acid)

PLA is a linear aliphatic thermoplastic polyester produced from renewable resources having excellent properties comparable to commercial petroleum-based plastics, which is of great interest to the packaging industry.\textsuperscript{37–42} PLA can be produced by two polymerization methods; (1) direct-polycondensation of lactic acid and (2) ring-opening polymerization of lactide, a dimer of lactic acid. The latter method is commercially utilized for PLA manufacturing due to economical production of high molecular weight polymers (greater than \(\sim 100,000\) g/mol).\textsuperscript{43–45} The semicrystalline PLA exhibits both \(T_g\) and \(T_m\) from thermal analysis. Above \(T_g\) (\(\sim 58^\circ\text{C}\)) PLA is rubbery, while below \(T_g\) it becomes a glass which is still capable to creep until it is cooled to its \(\beta\) transition temperature at approximately \(-45^\circ\text{C}\), which it behaves as a brittle polymer.\textsuperscript{46}

Unoriented PLA exhibits brittle property but possesses good strength and stiffness. Oriented PLA provides better performance than oriented polystyrene (PS) which is comparable to PET.\textsuperscript{47} Tensile and flexural moduli of PLA are higher than high density polyethylene (HDPE), polypropylene (PP) and PS, but the Izod impact strength and elongation at break values are lower than those polymers.\textsuperscript{48} Overall, PLA possesses the required mechanical and barrier properties desirable for a number of applications to compete with existing petroleum-based polymers.
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1.3 Poly(butylene succinate)

Poly(butylene succinate) (PBS) is one of the most interesting biodegradable polymeric materials. PBS is synthesized by polycondensation of succinic acid and 1,4-butandiol. Succinic acid is typically produced in microbes in the metabolic tricarboxylic acid cycle used for energy production. In view of this potential, a great effort is being developed to obtain succinic acid at low cost from renewable resources like starch, glucose or cellulose.\(^49\) Moreover, 1,4-butanediol could be easily obtained by reduction of succinic acid,\(^50–53\) thus giving access to a fully bio-based PBS. Aliphatic polyesters can be naturally degraded into the natural environment by bacteria and fungi.\(^54\) PBS has many excellent properties, including biodegradability, melt processability, chemical resistance and compostability.\(^51,52,55–56\) However, with further development of PBS, it is expected to be applied in the engineering fields, such as in automotive components, electrical and electronic industry due to ecological and economic advantages.\(^53,57\) Therefore, modification of PBS for plastic process application is needed. The currently reported of PBS modification methods include copolymerization, blending and compositing. PBS-based random or block copolymers have been widely studied and developed as green materials due to its biodegradability, good thermal stability and excellent mechanical properties.\(^58–61\)

1.4 Poly(butylene succinate-co-butylene adipate)

Poly(butylene succinate-co-butylene adipate) (PBSA) is one of the promising aliphatic thermoplastic polyesters with a range of desirable properties including biodegradability, melt processability, good mechanical properties and both thermal and chemical resistance.\(^62\) PBSA is a random copolymer
synthesized by polycondensation of 1,4-butanediol in the presence of succinic and adipic acids. Recent developments in fermentation technology have made it possible to produce new bio-based monomers. PBSA, compared with PBS, is more susceptible to biodegradation both because of its lower crystallinity and the greater flexibility of its polymer chains.  

1.5 Plasticizers

Plasticizers are an important class of low molecular weight non-volatile compounds that are widely used as additives in polymer industries. The primary role of plasticizer is to improve the flexibility and processability of polymers by lowering the second order transition temperature, the glass transition temperature ($T_g$). The council of the IUPAC (International Union of Pure and Applied Chemistry) defined a plasticizer as “a substance or material incorporated in a material (usually a plastic or elastomer) to increase its flexibility, workability, or dispensability”. These substances reduce the tension of deformation, hardness, density, viscosity and electrostatic charge of a polymer, at the same time increase the flexibility, resistance to fracture and dielectric constant of the polymer chain. Other properties of matrix material are also affected, such as degree of crystallinity, optical clarity, electric conductivity, fire behavior and resistance to biological degradation, amongst other physical properties. Plasticization is often used for the modification of biodegradable polymers to improve their processability and/or other properties demanded by a specific application. Plasticizers exchange the intermolecular bonds among polymer chains to bonds between the macromolecules and the small molecular weight compound thus promoting conformational changes.
resulting in increased deformability. Both the glass transition and the processing temperature of the material decrease, thus enabling the melt processing of heat-sensitive polymers at lower temperatures. Plasticizers used for PLA comprise of low molecular weight compounds such as oligomeric lactic acid, glycerol, triacetin, citrates, partial fatty acid esters, and blending PLA with various polymers as plasticizers such as thermoplastic starch (TPS), poly(ethylene oxide), poly(ethylene glycol) (PEG), poly($\varepsilon$-caprolactone), poly(vinyl acetate), to improve the PLA flexibility.

1.6 Nucleating Agents

Nucleating agents are often added to polymer matrix to improve the crystallization behavior. The crystallization temperature, the crystallinity and the crystallization rate increase with the nucleating agent effect. Talc qualifies as good reinforcement filler of polymeric matrices because it is a layered mineral with a high aspect ratio (particle diameter/thickness $\approx 20:1$). This is a consequence of its platy nature, having micron-sized dimensions on length and width, with nanometric thicknesses. Talc has an ideal formula of $\text{Mg}_3(\text{Si}_4\text{O}_{10})(\text{OH})_2$; its elementary structure is comprised of an octahedral magnesium hydroxide sheet ($\text{Mg}_{12}\text{O}_{12}\text{H}_4$) sandwiched between two tetrahedral silica sheets ($\text{SiO}_2$), in order to form talc layers that are superimposed indefinitely. The size of an individual talc platelet (a few thousand of elementary layers) can vary from approximately 1 to over 100 $\mu$m, depending on the conditions of ore formation. The Van der Waals’ gaps (interlayer or gallery) between the layers are formed due to stacking, which may assist in the delamination behavior of talc particles during the blending with TPS. Layer
charge is zero or very small, as there are not ions present between layers.\textsuperscript{70}

1.7 The Purpose of This Study

Poly(lactic acid) (PLA) is one of the biobased and degradable aliphatic polyesters.\textsuperscript{71,72} PLA is attracting increased attention for applications that require a biodegradable plastic because in a suitable disposal site it will degrade to natural products.\textsuperscript{55–77} It also has good physical properties such as high strength, thermoplasticity, and fabricability. However, its application is limited due to high price in comparison with polyolefins, low heat distortion temperature (HDT) and brittleness.\textsuperscript{78} To improve the mechanical properties of PLA various investigations have been studied by copolymerization with other monomers. However, these copolymerization processes is not yet economically viable and none is known to produce copolymers on an industrial scale for packaging applications.\textsuperscript{79} Blending PLA with other polymers/copolymers has also been investigated but only moderate improvement in mechanical properties was achieved.\textsuperscript{80–89}

The main conversion methods for PLA are based on melt processing. This approach involves heating the polymer above its melting point, shaping it to the desired forms, and cooling to stabilize its dimensions. Thus, understanding of thermal, crystallization, and melt rheological behaviors of the polymer is critical in order to optimize the process and part quality. Applications of melt processed PLA are injection molded disposable cutlery, thermoformed containers and cups, injection stretch blown bottles, extruded cast and oriented films, and melt spun fibers for nonwovens, textiles and carpets.\textsuperscript{90–92} PLA also finds uses in other less conventional applications such as housing of computers and electronic apparatus.
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and appliances. Recently, PLA has also been processed in conjunction with other filler materials to form composites which possess various unique properties, including those based on nanoclays, biofibers, glass fibers and cellulose.

To improve the mechanical properties of PLA and polymer blends the understanding of mechanism of additives is the most important parameter in the blend system. This doctor thesis involves the study of modification of PLA for future applications using processing techniques of blending of PLA and other biodegradable polymers including poly(butylene succinate) (PBS) and poly(butylene succinate-co-adipate) (PBSA). The effect of additives such as poly(ethylene glycol, PEG) and talcum on the property of polymer blends was investigated. The research study was divided into 3 parts.

Chapter 2, the author has prepared the PLA/PBSA blends, mixture of biobased and biodegradable polymers with a good impact resistance. The author investigated various aspects of the thermal, rheological, and mechanical properties in these blend systems and products such as the compression molded parts and the melt-spun fibers.

Chapter 3, the effect of plasticizer additive, poly(ethylene glycol) (PEG), to the property of polymer blends of PLA/PBS was investigated. Plasticizers are widely used to improve processability, flexibility and ductility of polymers. Many investigations reported the excellent plasticizing abilities of PEG when blended with PLA. Blending with low molecular weight PEG improves elongation at break and softness. The amount of PEG introduced in PLA has to be lower or equal to 20 wt% in each to avoid phase separation. However, the study of plasticizer on polymer blends of PLA and PBS has not been reported.
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The PLA/PBS blends were prepared, mixture of biobased and biodegradable polymers, with addition of PEG as a plasticizer. The author investigated various aspects of the thermal, rheological, and mechanical properties in these blend systems and products such as the compression and injection molded parts.

Chapter 4, Effect of talcum on the crystallinity of polymer blends of PLA/PBS was studied. Talcum is usually used as a nucleating agent and filler for biobased and biodegradable polymers to improve the polymer crystallinity as well as the mechanical property. However, the effect of addition of talcum to the blends of biodegradable polymers has not been discussed. For the polymer blend of PLA/PBS the phase separation of polymer blend and the difference property of each components affects their crystallinity due to addition of talcum.
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Chapter 2

Compression Molding and Melt-spinning of the Blends of Poly(lactic acid) and Poly(butylene succinate-co-adipate)

2.1. Introduction

Plastics have been widely used as basic materials in various industries due to their excellent characteristics and a low cost. Because of these profits, a huge amount of plastics which mostly made from fossil resources have been produced every year and a generation of large quantity of carbon dioxide has been promoting the global warming. Furthermore, the increase in the plastics waste quantity has caused various severe environmental problems. One way to solve these problems is replacing the commodity synthetic polymers with biobased polymers which can be produced from natural resources such as sugar and starch. Among various kinds of biobased plastics developed, poly(lactic acid) (PLA) is the most promising polymer due to its excellent mechanical properties and processability.1–3

PLA is a linear aliphatic thermoplastic polyester with excellent properties comparable to many petroleum-based plastics produced from renewable resources which is of great interest to the packaging industry due to its availability.4–9 PLA has an excellent processability and can be molded into a variety of products using conventional equipment applicable to polyolefins.10 It has high mechanical properties, thermal plasticity, and the processability. This plastic has been used for service ware, grocery, waste-composting bags, mulch films, controlled release matrices for fertilizers, pesticides, and herbicides owing
to wonderful characteristics described above. However, some of other properties such as the impact strength, heat distortion temperature (HDT), and gas barrier properties are frequently inadequate for various end-use applications. PLA has mostly been used for biomedical applications such as drug delivery systems and controlled release matrices for fertilizers, pesticides and herbicides. Despite its good properties, the applications are limited due to its low flexibility and low impact strength. To improve the flexibility and the impact strength of PLA, blending of the soft polymers, copolymerization and reactive extrusion techniques have been utilized. Some of these blends were found to be immiscible, resulting in poor mechanical properties. PLA is an aliphatic polyester with one of the highest melting temperatures of around 160–180°C. Generally a polymer having a lower melting temperature is more susceptible to biodegradation than one having a higher melting temperature because it has more flexible molecular chains which can fit into the active sites of enzymes. On the other hand, poly(butylene succinate-co-adipate) (PBSA) is a commercially available aliphatic polyester synthesized from diacids and diols. PBSA has a high flexibility, an excellent impact strength, a good melt processability, thermal and chemical resistances and low melting point around 90°C, and is more readily biodegradable than PLA.

In this chapter, PLA/PBSA blends were prepared, mixture of biobased and biodegradable polymers with a good impact resistance. The author investigated various aspects of the thermal, rheological, and mechanical properties in these blend systems and products such as the compression molded parts and the melt-spun fibers.
2.2. Experimental

2.2.1. Materials

The commercial PLA (PLA 2002D, NatureWorks LLC, MN) in a pellet form having a density of 1.24 g/cm³ with a glass transition temperature and a melting point of 52 and 155°C, respectively. The PBSA (Bionolle 3001 MD) was purchased from Showa Denko Co. (Tokyo, Japan) in a pellet from having a density of 1.23 g/cm³ with a glass transition temperature and a melting temperature of –45 and 94°C, respectively.

2.2.2. Compounding of PLA and PBSA blends

The blends of PLA and PBSA were compounded using a twin-screw extruder (CTE-D20L800, CHAREON TUT Co., Samutprakarn, Thailand). It has five controlled temperature zones which were set to the temperatures ranging at 100, 150, 160, 170, and 130°C. The screw speed was maintained at 80 rpm for all runs. Before extrusion, PLA and PBSA resins were dried at 80°C for 8 hours in an oven in order to remove any trace of moisture to prevent potential hydrolytic degradation during the melt processing in the extruder. The pellets of PLA and PBSA were manually premixed by tumbling in a high speed mixing, and subsequently fed into the extruder for melt compounding. The weight ratios of PLA and PBSA blends in this study are summarized in Table 2.1. The extrudate was quenched in a water bath and subsequently granulated by a pelletizer.

Table 2.1 The weight ratios of PLA and PBSA blends

<table>
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<tr>
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<th>100/0</th>
<th>90/10</th>
<th>80/20</th>
<th>70/30</th>
<th>60/40</th>
<th>50/50</th>
<th>0/100</th>
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<td>100</td>
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<td>80</td>
<td>70</td>
<td>60</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>PBSA</td>
<td>0</td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>40</td>
<td>50</td>
<td>100</td>
</tr>
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2.2.3. Sample Preparation

2.2.3.1 Compression Molding Process

PLA, PBSA and the polymer blends were dried at 80°C in the oven for 8 hours before subjected to compression molding process (LP-160T, Lab Tech Engineering Co., Samutprakarn, Thailand). The molding temperatures for neat PLA and the blends were 200°C for 7 min. The neat PBSA was compressed at 130°C. After holding time the molded specimens were cooled to room temperature for 10 min before removal from the mold.

2.2.3.2 Melt Spinning Process

Melt spinning of PLA, PBSA and their blends were carried out by using a laboratory size screw extruder equipped with a mono-hole die of 1.0 mm in inner diameter setting the die temperature at 180°C for PLA and blends and at 105°C for PBSA. The extrudate was taken up on the bobbin placed about 3 m below the die. Fibers with a mean diameter of about 100 μm were obtained. Fibers obtained were then drawn at 70 and 90°C, temperatures below the T_m of PBSA and the vicinity of the T_m of PBSA, respectively, by using a drawing machine consist of a pair of rolls rotating at different speed and a heating chamber. Fibers drawn at 70°C to × 4 were annealed at 75 and 100°C for 10 min.

2.2.4. Measurements and Observation

2.2.4.1 Rheology Property

Dynamic viscosity of the sample melts were measured by using a parallel plate type rheometer (MR-300, Reoroji Co. Kyoto Japan) at 160, 180 and 200°C in an angular frequency range from 0.1 to 4.0 radian/sec. Diameter of the plates was 18.0 mm and the gap between the plates was set at 1.0 mm. Dynamic
mechanical analysis measurements were performed using a rheometer (Reogel-E4000, UBM Co. Kyoto Japan) in a tensile mode over a temperature range from –50 to 200°C. Data acquisition and analysis of the storage modulus (E’), loss modulus (E”), and loss tangent (tanδ) were recorded automatically by the system. The heating rate and frequency were fixed at 3°C/min and 32 Hz, respectively. Films for DMA experiments 0.5 mm thick were prepared by using a compression molding machine.

2.2.4.2 Morphology

The morphology of the fracture surface of the blends were investigated using a scanning electron microscope (JSM-6510, JEOL Ltd., Tokyo Japan) operated at 10 kV. The specimens were fractured under cryogenic condition in liquid nitrogen and the fracture surface was sputtered with a thin gold layer. The specimens were mounted on a SEM stub using a double-side tape.

2.2.4.3 Thermal Property

The thermal property of the samples were studied by using a differential scanning calorimetry (DSC 8000, Perkin Elmer, MA) under N₂ atmosphere at heating rate of 10°C/min. The sample 5–8 mg was placed into alumina crucibles. After the first heating from –50 to 200°C at a rate of 10°C/min and held at that temperature for 5 min, then cooled to –50°C with cooling rate of 10°C/min before the second step where the samples were heated again and thermograms for second heating were recorded. Glass transition temperature (\(T_g\)), cold crystallization temperature (\(T_c\)), melting temperature (\(T_m\)), and the heat of fusion (\(\Delta H_m\)) were determined from the second heating scans.
2.2.4.4 Higher-Order Structure

Wide-angle X-ray diffraction (WAXD) patterns were obtained at room temperature using a nickel-filtered CuKα radiation of the wave-length 0.1542 nm, from a CN4037A1 (Rigaku Co. Tokyo Japan) sealed beam X-ray generator operating at 40 kV and 20 mA. The distance between sample and camera was 63 mm.

2.2.4.5 Mechanical Property

The tensile properties of the compression molded samples were determined according to ASTM D 638 (Type I) using dumbbell shape specimens. The test was carried out on a universal testing machine LR 10K Plus, LLOYD Instruments, West Sussex UK( with a crosshead speed of 10 cm/min. The Izod impact strength was determined according to ASTM D256 by using the Impact Tester (GT 7045, GOTECH Testing Machine Inc., Taiwan). The report value was the average of three replicates for each property test.

The tensile property of the fibers was determined by using a tensile testing apparatus (STA-1150, Orientec Co., Tokyo Japan) at a room temperature. Tensile speed was set at 50 mm/min. Tensile stress was obtained as a function of the strain and the tensile modulus, tensile strength and the elongation at break were determined. The data of 5 measurements were averaged for each sample.

2.3. Results and Discussion

2.3.1. Rheological Properties

Figure 2.1 shows the frequency dependences of the dynamic viscosity of PLA, PBSA and their blends measured at 160°C. All the sample melts showed a shear thinning behavior typical for the polymer melts. PLA showed a stronger
Chapter 2

shear thinning while PBSA showed a Newtonian region in a wide frequency range. It should be noted that the viscosity-frequency curve of the samples do not cross in a frequency range measured and the PLA has the highest viscosity and the PBSA has the lowest viscosity.

![Figure 2.1](image)

**Figure 2.1** Dynamic viscosity, $|\eta^*|$ of PLA, PBSA, and their blends as a function of the angular frequency, $\omega$ measured at 160°C.

Figure 2.2 (a) and (b) show the dynamic viscosity of PLA, PBSA and their blends measured at various temperatures at two different angular frequencies, 1.0 and 10 r/s, respectively. It is shown that the melt viscosity decreases with increasing amounts of PBSA irrespective of the temperature of the measurement and the angular frequency as well as with increasing temperature.
Figure 2.2 Dynamic viscosity, $|\eta^*|$ of PLA, PBSA and their blends at (a) $\omega = 1.0$ r/s and (b) 10.0 r/s measured at various temperatures.
2.3.2. Morphology

The morphology of the fractured surfaces of compression molded samples was investigated with high-resolution scanning electron microscopy (SEM). It is clearly seen from the fractured surface morphology shown in Figure 2.3 that the fractured surface of PLA (a) is rather smooth indicating that the sample was fractured in a brittle manner below its $T_g$. On the other hand, PBSA (f) has a rough surface which indicates a ductile fracture, PBSA was stretched before it was broken. Although all the blends have a sea and island morphology, the phase morphology depends on the blend ratios. The blends PLA/PBSA = 90/10 (b) and 80/20 (c) showed small particles or holes mostly less than 5 $\mu$m in diameter. These are the PBSA dispersing phase. On the other hand, PLA/PBSA = 70/30 (d) and 60/40 (e) showed fairly large PBSA dispersing phase around 10 $\mu$m or more in diameter. These results suggest that the PLA and PBSA were mixed well when PBSA content was low. However the size of the PBSA dispersing phase tended to be larger with increasing PBSA content. It has been known that the phase with a lower viscosity tends to be a continuous phase when the fractions of two phases are almost equal. However the PBSA is minor component in PLA/PBSA = 70/30 and 60/40 so that the PBSA phase was not disperse well in PLA phase. These differences in the phase morphology would affect the mechanical property of the blends. In general, in an immiscible binary polymer blend, the size of the dispersed phase increases as a function of the concentration of the minor phase in the blend, due to coalescence phenomena.
Figure 2.3 Fracture surfaces of PLA (a), blends (b)–(e), and PBSA (f).
2.3.3. Thermal Properties

DSC heating curves for the PLA, PBSA and the blends are presented in Figure 2.4. PLA showed a small and a sharp endothermic peak around 52 and 155°C, respectively. Since these peaks were also observed in the DSC curves of the blends, the peak at a lower temperature can be attributable to the $T_g$ and that at higher temperature may be $T_m$ of PLA. The $T_m$ and $T_g$ of PLA observed for the blends did not change with the content of PBSA significantly suggesting that the PLA and PBSA are incompatible and the PBSA phase dispersed in PLA matrix did not affect the crystallization of PLA. PBSA showed an exothermic peak followed by double endothermic peaks in the DSC curve. The exothermic peak is attributable to the crystallization of PBSA. The endothermic peak at a lower temperature may be attributed to re-melting of newly crystallized PBSA during heating in the DSC measurement and that at a higher temperature may be melting of PBSA crystal originally formed in the sample.\textsuperscript{21,22}

![Figure 2.4 DSC 2nd heating curve of PLA, PBSA and their blends.](image-url)
Chapter 2

PLA/PBSA samples showed an inflection point around 55°C attributable to the $T_g$ of PLA, an exothermic peak attributable to the crystallization of PLA around 100°C, and double endothermic peaks at higher temperature range. Again the endothermic peak at a lower temperature may be a melting of the PLA crystallized during the heating process of the DSC measurement and that at a higher temperature may be attributable to the melting of PLA originally exist in the sample.

Various parameters of the thermal property of PLA, PBSA and their blends are listed in Table 2.2 Here $\Delta H_m$ is a heat of fusion calculated form the endothermic peak area of the samples and $\phi_s$ are the fractions of the component polymers. The enthalpy of fusion of PLA phase in the blends, $\Delta H_m/\phi_{PLA}$, is almost constant at 30 J/g, indicating that the blend of PBSA phase did not affect the degree of PLA crystal in the blends significantly. On the other hand, the enthalpy of fusion of PBSA phase, $\Delta H_m/\phi_{PBSA}$, increases with PBSA content significantly. Especially, the blends PLA/PBSA = 90/10 and 80/20 showed a very low enthalpy of fusion. As described already, the PBSA phases in these blends are finely dispersing in the PLA matrix. It may be suggesting that the crystallization of PBSA is suppressed in the small restricted volume.
Table 2.2 Thermal properties of PLA, PBSA and their blends.

<table>
<thead>
<tr>
<th>PLA/PBSA</th>
<th>$T_m^{a}$ (PLA) (°C)</th>
<th>$T_g^{b}$ (PLA) (°C)</th>
<th>$T_m$ (PBSA) (°C)</th>
<th>$T_c^{c}$ (PLA) (°C)</th>
<th>$\Delta H_m^{d}$ (PLA) (J/g)</th>
<th>$\Delta H_m/\phi_{PLA}$ (J/g)</th>
<th>$\Delta H_m$ (PBSA) (J/g)</th>
<th>$\Delta H_m/\phi_{PBSA}$ (J/g)</th>
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<td>92.7</td>
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<td>55.2</td>
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</tbody>
</table>

$^{a}$ $T_m$, melt temperature of PLA and PBSA

$^{b}$ $T_g$, glass transition temperature of PLA

$^{c}$ $T_c$, crystallization temperature of PLA

$^{d}$ $\Delta H_m$, heat of melting of PLA and PBSA

$\phi_s$ are the fractions of the component polymers.
2.3.4. Mechanical Properties

2.3.4.1 Compression Mold Part

Figure 2.5(a–c) shows the tensile property of the compression molded samples. The tensile strength decreased monotonically with PBSA contents. Since the pure PBSA has much lower tensile strength than that of PLA and PBSA is dispersing phase, PBSA did not reinforce the PLA matrix. Tensile modulus is also a roughly decreasing function of PBSA content. This may be attributed to the much more elastic characteristic of PBSA dispersing phase. The elongation to break was almost constant irrespective of the PBSA content. Although the PBSA component exhibited a much higher elongation to break, this component was broken immediately after the breakage of PLA component.

Impact strength of the blends with PBSA content was shown in Figure 2.5(d). The brittle character of the PLA was modified by the blending of ductile PBSA as a minor phase. Especially the impact strength increased with PBSA content up to 20 wt%. As already described in the previous section, PBSA is well dispersing in PLA matrix in the blends PLA/PBSA = 90/10 and 80/20. The impact characteristics was modified by the finely dispersing PBSA phase in these blends. However the improvement of the impact characteristics was weaker with increasing PBSA content. This may be due to the poor mixing state of these blends. It has been known that the ductile phase finely dispersing stops the development of the fracture of the brittle matrix by absorbing the fracture energy. When the size of this dispersing phase increases, the improvement of the impact strength is less effective. This seems to be a reason why the blends with lower PBSA contents have higher impact strength. The small particle size is a clear and distribution of the dispersed phase indication of improved interfacial interactions and mechanical property.\textsuperscript{23}
Figure 2.5 Tensile strength (a), modulus (b), elongation to break (c), and impact strength (d) of Compression molded samples.
2.3.4.2 Fiber

1) Effect of Drawing Temperature

Figure 2.6 shows the effect of the drawing temperature on the mechanical property of the fibers. Both PLA and PBSA are in a solid state at 70°C. However the PBSA is in molten state at the temperature higher than 90°C although PLA is still in a solid state. All the as-spun fibers showed a fairly low tensile strength irrespective of the PBSA content and the tensile modulus decreased with increasing PBSA content reflecting the rubbery characteristics of PBSA phase. The drawing of the fiber at 70°C made a significant increase in both tensile strength and modulus. This improvement is mainly due to the molecular orientation of both PLA and PBSA phase to the fiber direction. The stretching of PBSA dispersing phase into fibrous shape may also be a reason for the improvement of the mechanical property.

The drawing of the fiber at 90°C gave a smaller effect, because the PBSA phase was in a molten state and the molecular orientation was given only to the PLA phase. Both the tensile strength and the modulus of the fibers drawn at 90°C decreased with the PBSA content. The drawing decreased the elongation to break irrespective of the drawing temperature. The elongation to break of the fiber seems to be governed only by the mechanical property of the PLA phase.
Figure 2.6 Mechanical property of the fibers drawn x 4 at 70 and 90°C as a function of the PBSA content.
2) Effect of Draw Ratio

Figures 2.7(a) and (b) compare the effect of the draw ratio of the mechanical properties of the fibers drawn at 70 and 90°C. The tensile strength and the modulus tended to increase and the elongation to break decreased with increasing draw ratio regardless of the drawing temperature. The mechanical property of the fibers drawn at 70°C seems to be effectively improved. This may suggest that the drawing at a lower temperature gives the molecular orientation more effectively. However the draw ratio achieved was much higher at 90°C and the fibers drawn to 8 times at 90°C showed a significantly improved mechanical property.

3) Effect of Annealing

Figure 2.8 shows the effect of annealing temperature on the mechanical property of the fiber drawn to 4 times at 70°C. The results indicate that the annealing of the fiber after drawing did not give a significant effect on the mechanical property regardless of the annealing temperatures.

WAXD patterns of as-drawn and annealed fibers are shown in Figure 2.9. As-drawn fibers show a spot-like but rather broad reflection from (110)/(200) of PLA on the equator. Further the blend fibers show ring-like reflections from PBSA. Upon annealing, PLLA molecules crystallized without relaxing the orientation. Another reflection from (203)/(113) can be observed on the third layer as well as a sharp reflection from (110)/(200) indicating typical uniaxial orientation of PLA phase. However the reflection from PBSA are very weak and almost disappeared. These results suggest that the PBSA phase in the blend fiber does not give any improvement on the mechanical property.
(a) PBSA content (wt%) vs. Tensile strength (MPa) and Tensile modulus (GPa) for samples drawn at 70°C. The graphs show the effects of PBSA content on tensile properties, with different symbols representing different treatment conditions: x 2 at 70°C, x 4 at 70°C, and x 5 at 70°C. The undrawn condition is also included for comparison. The elongation to break (%) is plotted against PBSA content (wt%) with similar treatment conditions indicated.

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Figure 2.7 Effect of the draw ratio of the mechanical property of the fibers drawn at 70°C (a) and 90°C (b).
Figure 2.8 Effect of annealing of the mechanical property of the fibers annealed at various temperatures.
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Conclusion

Blends of PLA/PBSA with various ratios were prepared and the compression molded parts and the melt spun fibers were obtained. The blends showed a typical sea-island morphology. When the PBSA content was low, PBSA phase finely dispersed in the PLA matrix. On the other hand, when the PBSA content was high, the PBSA minor phase dispersed as large droplets. Mechanical properties of the compression molded parts were affected by the dispersion state of PBSA minor component in PLA matrix. Impact strength of the compression molded parts was also improved by the addition of soft PBSA. The improvement was pronounced when the PBSA phase was finely dispersed in PLA matrix. However, the mechanical property of the blend fibers was affected by the post-drawing condition as well as the PBSA content.

Figure 2.9 WAXD patterns of as-drawn and annealed blend fibers.
References


Chapter 3

The effect of poly(ethylene glycol) as plasticizer in blends of poly(lactic acid) and poly(butylene succinate)

3.1. Introduction

In recent years, the development of biodegradable polymers has attracted a great deal of interest. Aliphatic polyesters are among the most promising materials as high-performance environmentally friendly biodegradable plastics. Biodegradable polyesters have received considerable attention in recent decades. Owing to their biodegradability and biocompatibility, they were first intensively developed for biomedical applications. Poly(lactic acid) (PLA) is one of the most studied polymers of this family because it can be produced via the fermentation of renewable resources, such as cassava or corn starch. It also has good physical properties, such as high strength, thermoplasticity, and spinnability. However, the low deformation at break and high modulus limits the application of PLA as packaging materials. Attempts to improve the mechanical properties have focused on biocompatible plasticizers. To improve the thermal properties and processability of PLA, one approach is to blend PLA with biodegradable polymers with good mechanical and thermal properties. One of the biodegradable polymers with the potential to improve the PLA properties is poly(butylene succinate) (PBS). PBS is a biodegradable semicrystalline polymer synthesized from butanediol and succinic acid, which are both available from biobased renewable resources. PBS has excellent biodegradability, mechanical properties, good thermal properties, and processing capabilities.
However, the PLA and PBS blends (PLA/PBS blends) still have some limitations, such as poor ductility or stiffness. To improve the ductility of PLA-based materials, many investigations have attempted to modify the PLA properties via plasticization.\textsuperscript{17} Blending with low molecular weight poly(ethylene glycol) (PEG) improves the elongation at break and softness.\textsuperscript{8,9,18–21} The amount of PEG introduced into PLA has to be lower than or equal to 20 wt\% to avoid phase separation. This limitation reduces the potential impact of PEG on the glass transition temperature ($T_g$) of PLA.\textsuperscript{21,22} However, the effect of PEG on the PLA/PBS blends has not yet been reported, i.e., thermal and mechanical properties and whether the PEG in PLA/PBS blends acts the same in PLA and PBS.

In this chapter, various aspects of the thermal, rheological, and mechanical properties of the PLA/PBS blends by adding PEG were investigated. Furthermore, the properties of the products, such as the compression and injection of molded parts, were also evaluated.

### 3.2. Experimental

#### 3.2.1. Materials

Poly(lactic acid) (3052D, Natureworks LLC, MN, USA) with $M_n$ and $M_w$ of $1.4 \times 10^5$ and $2.1 \times 10^5$ g/mol, respectively, and poly(butylene succinate) (FZ91PD, Mitsubishi Chemical Co. Tokyo, Japan) with $M_n$ and $M_w$ 3.6 $\times 10^4$ and 6.4 $\times 10^4$ g/mol, respectively, were used in this study. Poly(ethylene glycol) (Merck Co., NJ, USA) has a $M_w$ about 4,000 g/mol.
3.2.2. Compounding

The pellets of PLA and PBS were dried in an oven at 80°C in vacuo for 8 h prior to the melt processing. The blending weight ratios of each component (PLA:PBS) were 90:10, 80:20, 70:30 and 60:40. 2, 6 and 10 parts per hundred resin (phr) of PEG were mixed into the blends in a twin screw extruder (CTE-D20L800, L/D = 40, D = 20 mm, CHAREON TUT Co., Samutprakarn, Thailand). The extruder was operated at 200°C and 60 rpm screw speed for the compounding.

3.2.3. Injection Molding

Blend pellets were dried again as the same condition above before injection molding (SM120, model AP 120T, Asian Plastic Machinery Co., Taoyuan, Taiwan) into dumbbells. The temperature setting of the injection molding machine was 220°C. The dumbbell of test specimens are as per ASTM D638 (25 × 197 × 3 mm) for tensile testing, and ASTM D256 (63.5 × 12.7 × 3.2 mm) with a V-notch cut for Izot impact testing. Test specimens were conditioned for 48 h at 25°C before the measurement. PBS would be crystallized while PLA kept amorphous state in this condition.

3.2.4. Morphology

Observations of the phase morphology of the compounded strand and the fracture surface of the tensile specimens were carried out by scanning electron microscope (SEM) (JSM-S410LV, JEOL Ltd., Tokyo, Japan) operated at 15 kV. The strands extruded through a die of the twin screw extruder were fractured at liquid nitrogen temperature. The samples were fixed on supports and coated with gold.
3.2.5. Thermal Properties

The thermal properties of the samples were studied by use of a differential scanning calorimetry (DSC 8000, Perkin Elmer, MA, USA) under N₂ atmosphere at heating and cooling rates of 10°C/min. The samples (10 mg) were placed into alumina crucibles. After the first heating from –50 to 200°C, the sample was held at that temperature for 5 min, then cooled to hold at –50°C before a second heating step. The melting temperature ($T_m$), the heat of fusion ($\Delta H_m$) and the cold crystallization temperature ($T_c$) were determined from the second heating scans.

3.2.6. Rheological Properties

Dynamic mechanical analyses (DMA) were performed using a rheometer (Reogel-E4000, UBM Co., Kyoto, Japan) in a tensile mode over a temperature ranging from –50 to 200°C. Data acquisition and analysis of the storage modulus ($E'$), loss modulus ($E''$), and loss tanδ were recorded. The heating rate and frequency were fixed at 3°C/min and 32 Hz, respectively. Compression molded film samples 100 µm thick quenched from 200°C were prepared for DMA experiments.

3.2.7. Mechanical Properties

Tensile strength, Young’s modulus and elongation to break were determined according to ASTM method D638 under ambient conditions, using a tensile testing machine (LR10K Plus series, LLOYD Instrument, West Sussex, UK) at a cross head speed of 5 mm/min. The reported values were the average of at least 10 measurements.

Izod impact strength was determined according to ASTM method D256, using impact tester (Ceast 6545, Instron, Torino, Italy), and calculated by
dividing impact energy in Joule by the thickness of the specimen. Measurement were done at ten times for each point. The standard divisions were calculated and show the error bar in the figures.

3.3 Results and Discussion

3.3.1. Phase Morphology of the PLA/PBS Blend

Figure 3.1 shows the scanning electron microscope (SEM) images of the compounded strands with PLA:PBS ratios of up to 60:40. The fracture surfaces of neat PLA and neat PBS are fairly smooth and scale-like regardless of the PEG content. This is due to the brittleness of these materials at liquid nitrogen temperature. The blend PLA:PBS = 90:10 has many whitish spots less than 1 μm in size. The size of the white spots tended to increase with increasing PBS content indicating that they are likely a PBS-rich phase and most likely a phase separate PBS. The dark and whitish phases are closely adhered. PLA seems to be a continuous phase up to 10–40 wt% of PBS content and the addition of 10 phr PEG changed the phase morphology of PBS on PLA matrix which resulted in smaller particles of PBS. PEG reduced the surface energy of PBS and decreased the particle size. The results confirmed the role of PEG as a compatibilizing agent between PLA and PBS. Figures 3.1(5)a and 3.1(5)b of PLA/PBS blend with a ratio of 60/40 clearly shows the reduced particle size of PBS with the addition of PEG. The results are in agreement with the reduction and shift of $T_g$ of PLA close to that of PBS (Figure 3.4).

Figure 3.2(a) shows the second heating curves of neat PLA and of PLA blends that contain PEG. The first heating cycle to a temperature higher than the $T_m$ of the component polymers removed the uncertain thermal history of the
samples in the compounding process. Neat PLA showed $T_g$ around 60°C and a single melting peak around 160°C. Crystallization was not observed in the second heating cycle; thus, this single melting peak is due to the melting endotherm of the PLA that crystallized in the earlier cooling process. The addition of PEG slightly lowered the $T_g$ of PLA, and the presence of PEG inhibited the crystallization of PLA as suggested by the appearance of a cold crystallization peak. This indicated that the PEG enhanced the mobility of PLA chains. Interestingly, the melting endotherm of PEG-containing PLA showed two distinct peaks. As the crystallization of PEG-containing PLA occurred in the cooling and second heating process, the crystalline phases formed under these different conditions resulted in two melting peaks.
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(a) (b)

(1) (2) (3)
Figure 3.1 Phase morphology of PLA and PBS blends with PEG. The ratio of the PLA:PBS are (1) 100:0, (2) 90:10, (3) 80:20, (4) 70:30, (5) 60:40, and (6) 0:100. PEG was (a) not added, and (b) added at 10 phr.
3.3.2. Thermal Properties

Figure 3.2(b) shows the second heating curves of the PLA:PBS blend with a ratio of 60:40 containing between 0–10 phr of PEG. Similarly to the phenomenon observed in Figure 3.2(a), the blends containing PEG clearly showed the crystallization peak of the PLA phase. All curves showed the melting endotherm of PBS around 110°C. In the absence of PEG, there is no cold crystallization. The PLA phase crystallized during the cooling phase of the first heat-cool cycle. However, in the presence of PEG, cold crystallization peaks appear and are significant. This indicates that the presence of PEG significantly slows the crystallization rate of the PLA phase. The presence of separate melting and $T_g$ peaks in the differential scanning calorimeter (DSC) scans of the PLA and PBS phases clearly suggest that these are phase-separated blends.

Table 3.1 summarizes the thermal properties of the PLA/PBS blends with and without PEG, as measured by DSC. The addition of PEG did not affect the melting point of the PLA phase in the blends PLA:PBS = 60:40. The enthalpy of fusion of the PLA phase increased with increasing PEG content. The crystallization temperature ($T_c$) of the PLA phase decreased with increasing PEG content. The blending of PBS and PLA did not affect the thermal properties of the PLA phase.

The enthalpy of melting of the PLA crystals increases in the presence of PEG, although there is not much difference between samples with 2, 6, and 10 phr PEG. In the past, this has been attributed to the increase in the molecular mobility afforded by the plasticizer allowing for better chain packing. Moreover, this may be linked with the slower crystallization rate that affords time for chain
reordering. Judging by the $T_g$ values for neat PLA, neat PBS, and the 60:40 blends, there is little difference in $T_g$ with blending and, presumably, little miscibility between the phases. Likewise, there is little effect of blend composition on the $T_m$ values for both phases. However, the enthalpy of melting (crystallinity) of the PBS phase is affected (decreased) because of PLA when the PBS content in the blend is at or below 20 wt%. In contrast, the enthalpy of melting of the PLA phase is not affected by the presence of the PBS phase. The effect of PEG on the $T_g$ of the PLA phase is significant, whereas it has marginal effect on the $T_g$ of the PBS phase. The addition of PEG affects the melting temperature of the PBS phase but not that of the PLA phase.

DMA analysis gives clear information on the $T_g$ of the component polymers; therefore, the plasticizing efficiency was evaluated by measuring the change in $T_g$ as a function of PBS and PEG contents. Figure 3.3 shows the temperature dependence of the loss modulus ($E''$) of neat polymers and their blends without PEG. Neat PLA and PBS showed a very sharp $E''$ peak around 60°C and a rather broad and smaller peak around –20°C, respectively. The peaks of $E''$ may be ascribed to the movement of amorphous chains of PLA and PBS, and the peak temperature may be corresponding to $T_g$. Figure 3.3 shows that $T_g$ of PLA slightly shifts to a lower temperature and that of PBS shifts to a higher temperature with increasing PBS content, suggesting partial compatibility between PLA and PBS.
Figure 3.2 DSC trace of second heating scan of (a) neat PLA and (b) blends of PLA and PBS at a ratio of 60:40. The parts per hundred resin of PEG are shown above each curve.
Table 3.1 Thermal data of neat PLA, neat PBS, blends of PLA and PBS with PEG.

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The data were measured by DSC during the second heating at 10°C/min.

\(^1\) Parts per hundred resin of PEG.

\(^2\) The values were converted to per g of PLA by division of the weight ratio of PLA in PLA and PBS blends with PEG.

\(^3\) The values were converted to per g of PBS by division of the weight ratio of PBS in PLA and PBS blends with PEG.
Figures 3.4(a) and 4(b) compare the effect of PEG content on $T_g$ of PLA and PBS in neat component polymers and in PLA:PBS = 60:40 blends. Although $T_g$ of PLA phase in both the neat PLA and PLA/PBS blends decreased with the addition of PEG, the effect is stronger for neat PLA. The result indicates that PEG prefers to stay in PBS rather than PLA, which results in lower $T_g$ for PLA and higher $T_g$ for PBS when the PEG content is 10% in the PLA:PBS = 60:40 blend. In contrast, the effect of the addition of PEG on $T_g$ of PBS is rather weak because $T_g$ of PBS and PEG is in the same temperature range.

**Figure 3.3** Temperature dependence of log $E''$ for neat PLA, neat PBS and their blends without PEG.
Figure 3.4 The effect of PEG content in PLA and PBS blends (60:40) on $T_g$. (a) neat PLA and PLA phase in blends of PLA and PBS, and (b) neat PBS and PBS phase in blends of PLA and PBS, as measured by DMA.
3.3.3. **Mechanical Properties**

The higher the PBS ratio is in PLA:PBS blends, the lower is the tensile strength (Figure 3.5). The addition of PEG to PLA/PBS blends caused the tensile strength to decrease. The effect was stronger with increased PEG content. Amita *et al.* reported that the tensile strength and modulus of the PLA/PBS blends decreased with increasing PBS content but followed approximately the mixing rule for 90:10 and 80:20 blends.\textsuperscript{24} This means that some compatibility between PLA and PBS phases is possible when the PBS concentration is lower.

The Young’s modulus of PLA/PBS blends with PEG also show the same tendency to decrease with increasing PEG content (Figure 3.6). With different results the Young’s modulus and tensile strength of PLA/PBS blends with PEG show the same tendency to decrease with increasing PEG content in all compositions of the blends from 90:10 to 60:40 (Figure 3.6). The tensile strength of the blends approaches the values for PBS but higher than neat PBS indicates compatibilizing effect on PEG addition in the blends.
Figure 3.5 Tensile strength of blends of PLA and PBS with PEG. Measurements were done at ten times for each point. The standard deviations were very small to show on the figure.

Figure 3.6 Young’s Modulus of blends of PLA and PBS with PEG. Measurements were done at ten times for each point. The standard deviations were very small to show on the figure.
The elongation at break of PLA/PBS blends with PEG is shown in Figure 3.7. Neat PLA shows an elongation at break lower than that of neat PBS owing to PLA being a low-deformation-at-break material,\textsuperscript{15,17} whereas PBS is a high-flexibility material.\textsuperscript{25} The PLA:PBS blends with a ratio of 60:40 show higher elongation at break than other blend ratios at all PEG contents. The addition of PEG results in apparent plastic deformation behavior between the linear elastic deformation and necking region, indicating improved ductility.\textsuperscript{23,26} As mentioned above, PEG localized at the PLA phase in the PLA/PBS blends. Therefore, when comparing PLA:PBS blends with ratios of 90:10, 80:20, 70:30, and 60:40, the lower the PLA content is, the higher the concentration of PEG in the PLA phase is, which increases the toughness of the polymer.

The impact strengths of neat PLA and PBS and PLA/PBS blends with variable PEG contents are shown in Figure 3.8. The impact strengths of PLA/PBS blends with PEG slightly increased with the addition of PEG up to 10 phr PEG. However, 10 phr PEG decreased the impact strength of the blends compared to the 5 phr PEG blends. The PLA/PBS blends with ratios of 90:10, 80:20, 70:30, and 60:40 all showed similar results. In contrast, the addition of PEG increased the impact strength of pure PLA at all levels, whereas it reduced the impact strength of pure PBS.
Figure 3.7 Elongation at Break of blends of PLA and PBS with PEG.

The error bars means standard deviations for ten times measurement at each point.

Figure 3.8 Impact strength of blends of PLA and PBS with PEG. The error bars means standard deviations for ten times measurement at each point.
3.3.4. Fracture Surface

The morphology of the fractured surface of tensile specimens of PLA/PBS blends with and without PEG is shown in Figures. 3.9(a) and (b), respectively. The most compatible ratio of PLA:PBS is 80:20 with and without PEG addition. The morphology shows less clear phase separation compared to other blend ratios without PEG. The fracture surface of the tensile specimen of PLA:PBS with ratio of 80:20 and 10 phr PEG shows ductile fracture behavior. For neat PLA, the addition of PEG (Figure 3.9(1-b)) changed the fracture mode of PLA from brittle to ductile. Although neat PBS without PEG is ductile, PBS with PEG at 10 phr (Figure 3.9(6-b)) showed rather brittle fracture probably because of the agglomeration of PEG in the PBS phase. The blends without PEG show brittle fracture behavior up to 20 wt% of PBS in the blends. At higher PBS content, stretching of the PBS phase was observed. A similar morphology was observed up to 10 wt% of PBS with PEG, and fibrous morphology was observed at higher PBS content. These results suggest that the transition from brittle to ductile behavior occurs at lower PBS content when the blends contain PEG.

Conclusion

The addition of PEG to PLA/PBS blends results in a significant decrease in the $T_g$ of the PLA phase in these blends. Thermal analysis confirmed preferably migration of PEG to PLA phase than that of PBS. The PEG enhances mobility of PLA molecules. The mechanical property measurement of injection molded samples shows a decrease in Young’s modulus and tensile strength with an increase in PEG content. The mode of fracture of PLA in blends of PLA and
PBS changes from brittle to ductile fracture following the addition of PEG as illustrated by SEM imaging. The addition of PEG to PLA/PBS blends decreases $T_g$ of the PLA phase in these blends. Thermal analysis confirmed the migration of PEG to the PLA phase rather than PBS. PEG enhances the mobility of the PLA molecules. Injection molding samples show decreasing Young’s modulus and tensile strength with increasing PEG content. The fracture mode of PLA in blends of PLA and PBS changes from brittle to ductile following the addition of PEG, as shown in the SEM images. Morphological studies verified the phase separation of polymer components, while the addition of PEG affected the morphology of PBS phase on PLA matrix as a compatibilizing agent. At low PEG contents, a good distribution of polymer components and plasticizer resulted in high Izod impact strength.
Figure 3.9 Morphology of fractured surface of tensile specimen of blends of PLA and PBS with PEG. The ratio of the PLA:PBS blends are (1) 100:0, (2) 90:10, (3) 80:20, (4) 70:30, (5) 60:40, and (6) 0:100. PEG was (a) not added, and (b) added 10 phr.
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Chapter 4

Isothermal crystallization kinetics of talc-filled poly(lactic acid) and poly(butylene succinate) blends

4.1. Introduction

To accelerate the crystallization of poly(lactic acid) (PLA), the most effective and extensively used method is probably the incorporation of nucleating agents. Among the various types of nucleating agents, inorganic particles, such as talc and clay, have been widely used. Mohammadreza et al. reported that microsized talc particles effectively enhance the crystallization rate of PLA through fast nucleation and a high growth rate, leading to more perfect crystals. Poly(butylene succinate) (PBS) is a biodegradable semicrystalline aliphatic polyester having excellent mechanical properties, processing capabilities, and good potential to blend with PLA. The crystallization of polymers affects the properties of the products and the process control. Majority of the previous studies reported the effect of talc as a nucleating agent for polypropylene or neat PLA; however, the influence of talc on PLA and PBS (PLA/PBS) blends has not been reported. Crystallization speed has a profound effect on the productivity of injection molding. Further, the thermal deformation of the product is improved by crystallization. Therefore, it is essential to evaluate the crystallization kinetics of PLA/PBS blends.

In this study, we analyzed the effect of talc addition on the crystallization of neat PLA, PBS, and PLA/PBS blends, which were mainly evaluated with respect to the isothermal crystallization kinetics and spherulitic morphology.
4.2 Experimental

4.2.1 Materials

Poly(lactic acid) (3052D, Natureworks LLC, MN, USA) with $M_n$ and $M_w$ of $1.4 \times 10^5$ and $2.1 \times 10^5$ g/mol, respectively, and poly(butylenesuccinate) (FZ91PD, Mitsubishi Chemical Co. Tokyo, Japan) with $M_n$ and $M_w$ $3.6 \times 10^4$ and $6.4 \times 10^4$ g/mol, respectively, were used in this study. The grade of 3052D is L-form PLA and crystalline polymer. Talc powder with an average particle size of 1 µm was used (Imerys Talc Austria GmbH, Graz, Austria).

4.2.2 Preparation of samples

Pelts of PLA and PBS were dried in oven at 80°C. PLA, PBS, and PLA/PBS blends with weight ratios of 80:20 and 60:40 were dissolved in chloroform. The mixtures were stirred for 1 h before addition of talc and then stirred for 4 h until the mixture was completely dissolved. The amount of talc used ranged from 0.1, 0.5, 1.0 and 5.0 parts per hundred parts by weight of resin (phr). In this study resin means PLA, PBS, and PLA/PBS blends. The solutions were then casted on the petri dishes. After casting, the solvent was evaporated overnight at room temperature, and then the samples were dried in an oven at 80°C for 24 h.

4.2.3 Thermal properties

The overall isothermal melt crystallization kinetics were studied by using a differential scanning calorimetry (DSC) (DSC 8000, Perkin Elmer, MA, USA) under N$_2$ atmosphere at heating rate of 10°C/min. The samples (10 mg) were placed into alumina crucibles. After the first heating 30 to 200°C at a rate of 10°C/min, held at that temperature for 3 min, cooled to the chosen crystallization temperature ($T_c$) at 60°C/min, and held for a period of time until
the isothermal crystallization was complete. The exothermal traces were recorded for the later data analysis.

### 4.2.4 Polarized Optical Microscope

Spherulite morphologies of PLA, PBS and PLA/PBS were observed by a polarized optical microscope (POM) (DC4+156-S, National Optical and Scientific Instrument Inc., TX, USA) equipped with a digital camera (BX53, Olympus Co. Tokyo, Japan). The samples were placed between two cover glasses, melted and pressed at 220°C for 3 min on a Hot Stage (FP82HT, Mettler-Toledo Inc., OH, USA). Then they were quickly cooled to the desired temperature for isothermal crystallization. After the completion of crystallization, the spherulite morphologies were recorded.

### 4.2.5 Morphology

Observations of the phase morphology of the films were carried out by scanning electron microscopy (SEM) (JSM-S410LV, JEOL Ltd., Tokyo, Japan) operated at 15 kV. The films were fractured at liquid nitrogen temperature. The samples were fixed on supports and coated with gold.

### 4.3 Results and Discussion

#### 4.3.1 Isothermal Crystallization

During the injection molding process, the polymer was isothermally crystallized inside the preheated mold for a short time. The completion of crystallization is essential for obtaining high-performance PLA-based polymer blends. In this regard, we evaluated the isothermal crystallization of PLA, PBS, and PLA/PBS blends with the addition of 0.1, 0.5, 1.0, and 5.0 phr of talc. The relative crystallinity ($X_t$) versus crystallization time ($t$) for PLA, PBS, and...
PLA/PBS (with ratios of 80:20 and 60:40) at various temperatures were measured. $X_t$ is defined as the ratio of the absolute crystallinity and the crystallinity at the end of crystallization.\textsuperscript{10} Figure 4.1 shows typical DSC crystallization curves for PLA/PBS (60:40) at 80, 90, 95, 100, and 110°C with and without talc. The values of $X_t$ were estimated from the curves. In the same manner, we calculated $X_t$ for other blend ratios.

Figure 4.2(a) shows the relative crystallinity of PLA crystallized at 90°C as a function of time and talc content. The same is shown for PLA/PBS (80:20 and 60:40) and neat PBS in Figure 4.2(b–d), respectively. The analyses were performed in the temperature range from 90 to 125°C. The results of the analysis at 90°C are discussed as an example. All the curves in Figure 4.2 illustrate a sigmoid dependence on time. The crystallization of neat PLA at 90°C was completed within 120 min, whereas PLA with 0.1, 0.5, 1.0, and 5.0 phr of talc completely crystallized within 66, 60, 61, and 47 min, respectively (Figure 4.2(a)). The results are in contrast with those reported for zinc citrate nucleation by Song, et al.\textsuperscript{11} Crystallization at 90–125°C shows a similar tendency and reiterates that talc can be used to effectively enhance the isothermal crystallization of PLA. Neat PBS was completely crystallized within 6 min. Due to the rapid crystallization of PBS at 90°C, talc less than 1.0 phr has no effect on the crystallization rate. In contrast to the nucleated PLA, the completion of the isothermal crystallization of nucleated PBS requires a longer time to compare with the pure polymer. The crystallization rate of PBS decreased with increasing contents of talc at 95 and 100°C, which may be caused due to the hindrance to the movement of PBS molecular chains caused by talc at temperatures near the melting temperature.
Figure 4.1 A typical DSC crystallization curves for PLA/PBS (60:40) at (a) 80°C, (b) 90°C, (c) 95°C, (d) 100°C, (e) 110°C, and (f) 120°C with and without talc.
The Avrami equation is generally used to describe the isothermal melt-crystallization kinetics of polymers. According to the equation, $X_t$ changes with the crystallization time $t$ and is expressed as follows:

$$1 - X_t = \exp(-kt^n),$$

where $n$ is the Avrami exponent and $k$ is the crystallization rate constant, which involves both nucleation as well as growth rate parameters. The following

**Figure 4.2** Relative crystallinity with time of (a) neat PLA, (b) PLA/PBS (80:20), (c) PLA/PBS (60:40), (d) neat PBS at 90°C.
equation can be derived from the above equation.

\[ \ln(-\ln(1 - X_t)) = \ln k + n \ln t \]

Then, \( \ln(-\ln(1 - X_t)) \) can be plotted against \( \ln t \) to generate an Avrami plot.

The results of relative crystallinity of neat PLA, neat PBS, and PLA/PBS with and without talc (Figure 4.2) are plotted using the Avrami equation (Figure 4.3(a–d)).

**Figure 4.3** Avrami plots of (a) neat PLA, (b) PLA/PBS (80:20), (c) PLA/PBS (60/40), (d) neat PBS at 90°C.
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The values of $n$ and $\ln k$ were obtained from the slopes and intercepts of the vertical axis on the graph. The plots in accordance with above equation for neat PLA, neat PBS, and PLA/PBS at 90°C with and without talc are linear in either case (Figure 4.3). Further, the $n$ values were estimated from Figure 4.3 and are listed in Table 4.1. The $n$ values of neat PLA were one value smaller than those of neat PBS and PLA/PBS. Although it is difficult to decide the crystal growth dimensions form the $n$ values, it appears that the crystal uniformly grew in neat PBS and PLA/PBS, and nonuniformly in neat PLA.

<table>
<thead>
<tr>
<th>Talc (phr)</th>
<th>neat PLA</th>
<th>80/20</th>
<th>60/40</th>
<th>neat PBS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2</td>
<td>3</td>
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<td>3</td>
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<tr>
<td>0.1</td>
<td>2</td>
<td>4</td>
<td>3</td>
<td>3</td>
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<tr>
<td>0.5</td>
<td>2</td>
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<tr>
<td>1.0</td>
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<tr>
<td>5.0</td>
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</tbody>
</table>

Crystallization halftime ($t_{1/2}$) is defined as the time at which the crystallization process reaches 50%. The longer the $t_{1/2}$, the slower is the crystallization rate. The value of $t_{1/2}$ can be obtained using the following equation:

$$t_{1/2} = \left(\frac{\ln 2}{k}\right)^{1/n}$$

The $k$ values were estimated from Figure 4.3 and $t_{1/2}$ was calculated. The effect of talc on $t_{1/2}$ is shown in Figure 4.4. Since the crystallization speed of neat PLA was too slow at 80°C, the values cannot be plotted in Figure 4.4(a). In
contrast, neat PBS was in the molten state at the temperatures shown in Figure 4.4(e) and (f). The $t_{1/2}$ values for PLA/PBS (80:20) at 80°C are larger than those for neat PLA, PBS, and PLA/PBS (60:40). This is due to its high PLA content. Crystallization occurred in PLA/PBS (80:20) at 80°C, which is due to the crystallization of PBS. Although $t_{1/2}$ increases with talc content until 1.0 phr, $t_{1/2}$ decreases with the addition of 5.0 phr of talc because of the inhibition effect of talc on PBS, which is an interesting phenomenon. We reason that PLA is difficult to crystallize at this temperature but will be crystallized in the presence of large amounts of talc.

The $t_{1/2}$ value for neat PLA at 90°C decreased with increasing talc content, whereas the value for neat PBS gradually increased (Figure 4.4(b)). These phenomena can be seen more clearly at 95 and 100°C (Figure 4.4(c) and (d)). This implies that talc not only promotes the crystallization of PLA but also acts as a crystallization inhibitor for PBS.
Figure 4.4 Effect of the talc on the half-time crystallization at (a) 80°C, (b) 90°C, (c) 95°C, (d) 100°C, (e) 110°C, and (f) 120°C.
4.3.2 Morphology

The morphology was determined via POM. PLA produces spherulites, while PBS should be in the molten state at 120°C. At this temperature, the spherulite size decreases as the amount of talc in neat PLA (Figure 4.5) and PLA/PBS (60:40) (Figure 4.6) increases, which indicates that talc acts as a nucleating agent for PLA. On the other hand, the crystallization speed of PLA was too slow to be observed via POM under these operating conditions at 90°C. Therefore, only spherulites of PBS could be observed. At this temperature, the spherulite size increased with the amount of talc in neat PBS (Figure 4.7) and PLA/PBS (60:40) blend (Figure 4.8). This indicates that talc inhibits the crystallization of PBS. This information will be useful for improving the properties of PLA and PBS blends for various applications.
Figure 4.5 Polarized optical micrographs of neat PLA at 120°C with talc (a) 0 phr (b) 0.1 phr (c) 0.5 phr (d) 1.0 phr.

Figure 4.6 Polarized optical micrographs of PLA/PBS (60:40) at 120°C with talc (a) 0 phr (b) 0.1 phr (c) 0.5 phr (d) 1.0 phr.
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Figure 4.7 Polarized optical micrographs of neat PBS with at 90°C with talc
(a) 0 phr (b) 0.1 phr (c) 0.5 phr (d) 1.0 phr.

Figure 4.8 Polarized optical micrographs of PLA/PBS (60:40) at 90°C with talc
(a) 0 phr (b) 0.1 phr (c) 0.5 phr (d) 1.0 phr.
Conclusion

The effect of talc loading on the isothermal crystallization behavior of PLA/PBS blends was studied. The addition of talc to neat PLA, PBS, and PLA/PBS blends significantly enhanced the isothermal crystallization kinetics and spherulite morphology of PLA in the PLA/PBS blend relative to neat PLA. There was no effect of talc on the isothermal crystallization kinetics of PBS. However, the high content of talc inhibited the crystallization rate. The spherulite morphology indicated that the nucleation density of PLA spherulites in 80:20 (PLA/PBS) was greater than that of 60:40 blend. The isothermal crystallization results revealed that the overall crystallization rate is much faster in talc-nucleated PLA and PLA/PBS. The dependence of $t_{1/2}$ on isothermal crystallization temperature verified the effect of polymer components ratio in neat PLA/PBS and composites.
References

Chapter 5

General Conclusion

Poly(lactic acid) (PLA) is a representative of biobased and biodegradable polymer having potential for industrial applications to replace the fossil-base polymers. However, PLA has limited properties such as brittleness, low thermal stability, which is important for product manufacturing. The development of PLA-based polymers to improve their properties comprises of blending of PLA with polymer having appropriate properties or addition of additives to enhance the polymer processing and product properties. In this study PLA was blended with biodegradable polymers including poly(butylene succinate-co-adipate) (PBSA), poly(butylene succinate) (PBS) to improve the toughness and ductility of PLA. The blending of PLA with PBSA and PBS will produce the environmental friendly materials for polymer products. Furthermore, the addition of additives such as poly(ethylene glycol) (PEG) and talcum to the polymer blends with the purpose to improve the polymer property have been studied. This thesis comprises of 5 chapters. The introduction and purpose of this study is presented in Chapter 1 follows by the significance of research in Chapter 2 to 4 and the general overview is summarized in Chapter 5. The essence of each chapter of the thesis is as follows.

In Chapter 1, the overview of biobased and biodegradable polymers and their development including incomplete points for improvement of polymer properties compared to previous research are reported. The significance and purpose of modification of polymer blends of PLA and PBSA or PBS and the
understanding of mechanism of additives to the polymer blends are described.

In Chapter 2, compression molding and melt-spinning of the blends of PLA and PBSA was studied. Blends of PLA/PBSA with various ratios were prepared and the compression molded parts and the melt spun fibers were obtained. The blends showed a typical sea-island morphology. When the PBSA content was low, PBSA phase finely dispersed in the PLA matrix. On the other hand, when the PBSA content was high, the PBSA minor phase dispersed as large droplets. Mechanical properties of the compression molded parts were affected by the dispersion state of PBSA minor component in PLA matrix. Impact strength of the compression molded parts was also improved by the addition of soft PBSA. The improvement was pronounced when the PBSA phase was finely dispersed in PLA matrix. However the mechanical property of the blend fibers was affected by the post-drawing condition as well as the PBSA content.

In Chapter 3, the effect of PEG as plasticizer in blends of PLA and PBS was studied. The effect of PEG on the mechanical and thermal properties of PLA/PBS blends was examined. Overall, it was found that PEG acted as an effective plasticizer for the PLA phase in these microphase-separated blends, increasing the elongation at break in all blends and decreasing the $T_g$ of the PLA phase. Significant effects on other properties were also observed. The tensile strength and Young’s modulus both decreased with increasing PEG content in the blends. In contrast, the elongation at break increased with the addition of PEG, suggesting that PEG acted as a plasticizer in the polymer blends. Scanning electron microscope images showed that the fracture mode of PLA changed from brittle to ductile with the addition of PEG in the polymer blends.

In Chapter 4, blends comprising PLA, PBS, and talc were prepared via
Chapter 5

a solution casting method. The weight ratios of PLA to PBS (PLA/PBS) blends were 80:20 and 60:40, whereas the talc content was varied from 0 to 5.0 phr. The crystallization halftime \( t_{1/2} \) of PLA/PBS (80:20) at 80°C was higher than those of neat PLA, PBS, and PLA/PBS (60:40); this is due to its high PLA content. The \( t_{1/2} \) value for neat PLA at 90°C decreased when the talc content was increased, whereas the value for neat PBS gradually increased. These phenomena can be seen more clearly at 95 and 100°C. This means that talc not only promotes PLA crystallization but also acts as a crystallization inhibitor for PBS. The isothermal crystallization kinetics and spherulitic morphology of these samples were investigated. The extent of talc loading showed a strong dependence on the isothermal crystallization rate and the extent of PLA crystallinity, whereas the contrary effect was observed for PBS due to the growth of large crystals. This suggests that talc not only promotes the crystallization of PLA but also inhibits the crystallization of PBS. The results are in agreement with the crystallization halftime and polarized optical microscopy analysis.

The achievement of this study is considered to be superior in terms of using biobased and biodegradable polymers as starting materials for polymer packaging and fiber applications. The improvement of mechanical and thermal properties of PLA with polymer blends of PLA/PBSA and PLA/PBS and the understanding of thermal, crystallization, mechanism of the additives and melt rheological behaviors of the polymers have been successfully studied. These parameters are critical in order to optimize the process and product quality. The study outcome is expected to be significant for development of environmental friendly materials for polymer industry.
Publication List

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   DOI: 10.1007/s10965-016-1045-y
Other Publications


Presentations

1. “Preparation of Polymer Blends Between Poly(lactic acid) and Poly(butylene adipate-co-terephthalate) and Biodegradable Polymers as Compatibilizers” Weraporn Pivsa-Art, Amorn Chaiyasat, Sommai Pivsa-Art, Hideki Yamane and Hitomi Ohara, 10th Eco-Energy and Materials Science and Engineering Symposium (10th EMSES), Ubon ratchatthani, Thailand, December 5 to 8, 2012

2. “Effect of Additives on Thermal and Mechanical Properties of Polymer Blends of Poly(lactic acid) and Poly(butylene succinate-co-adipate)”, Sommai Pivsa-Art, Sorapong Pavasupree, Narongchai O-Charoen, Weraporn Pivsa-Art, Supaphorn Thumsorn, Hideki Yamane and Hitomi Ohara, 10th Eco-Energy and Materials Science and Engineering Symposium (10th EMSES), Ubon ratchatthani, Thailand, December 5 to 8, 2012

3. “Effects of Poly(ethylene glycol) on Polymer blends of Poly(lactic acid) and


8. “Biodegradable Composite Braided Yarn Reinforced With Natural Fibers”,
Sommai Pivsa-Art, Natee Srisawat, Rinlada Sirisangsawang and Weraporn Pivsa-Art, Thailand Research Expo 2015, Centara Grand & Bangkok Convention Centre at Central World, Bangkok, Thailand, August 16 to 20, 2015

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