

# Miscibility of Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) with High Molecular Weight Poly(lactic acid) Blends Determined by Thermal Analysis

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**ABSTRACT:** An important strategy used in the polymer industry in recent years is blending two bio-based polymers to attain desirable properties similar to traditional thermoplastics, thus increasing the application potential for bio-based and bio-degradable polymers. Miscibility of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) with poly(L-lactic acid) (PLA) were characterized using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). Three different grades of commercially available PLAs and one type of PHBV were blended in different ratios of 50/50, 60/40, 70/30, and 80/20 (PHBV/PLA) using a micro-compounder at 175°C. The DSC and TGA analysis showed

the blends were immiscible due to different stereo configuration of PLA polymer and two distinct melting temperatures. However, some compatibility between PHBV and PLA polymers was observed due to decreases in PLA's glass transition temperatures. Additionally, the blends do not show clear separation by SEM analysis, as observed in the thermal analysis. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 3074–3081, 2012

**Key words:** poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV); poly(L-lactic acid) (PLA); biomaterials; differential scanning calorimetry (DSC); thermogravimetric analysis (TGA)

## INTRODUCTION

Bio-polymers have generated vast interest in this decade due to rapid growth in consumer awareness and stricter government regulation of municipal waste.<sup>1,2</sup> Many researchers believe bio-polymers will adequately replace current thermoplastic polymers.<sup>3,4</sup> Currently, biodegradable plastics are either derived from naturally produced or synthesized from renewable resources.<sup>5</sup> Such polymers that are coming under considerations are poly(hydroxyalkanoate) (PHA) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) polyesters produced by fermentation process in plants and microorganisms, or poly(L-lactic acid) (PLLA) polyester derived from ring opening polymerization of bio-derived linear lactic acid residues from microbial fermentation.<sup>5</sup> These polymers are well known to have the ability to fully biodegrade in composting conditions due to their hydrolyzable backbones, thus potentially alleviating the waste disposal problem of diminishing landfill space.<sup>1,3,4</sup> In addition to being aliphatic polyesters, these polymers provide a range of mechanical

properties that can be manipulated from packaging to medical applications.<sup>1,3–6</sup>

Fermentation of agriculture crops and waste products yields lactic acid (2-hydroxypropionic acid), which is the basic building block for the poly(lactic acid) (PLA) polymer.<sup>7,8</sup> Commercially available high molecular weight PLA resins are copolymers of PLLA and poly(D-, L-lactic acid) (PDLA) produced from the ring opening polymerization of lactides.<sup>9</sup> The cyclic dimer of lactic acid, lactide, is produced by condensation of two lactic acid units resulting in three different stereo-isomers (D-, L-, and mesolactide).<sup>7,9</sup> In addition, the L-isomer is the main fraction of PLA resin, since majority of the lactic acid found in renewable resources exists in this isomeric form.<sup>9</sup> Therefore, a semi-crystalline structure results composed of three-carbon numbered repeating unit with hydroxyl and carboxyl groups at the end of structure.<sup>1,2,6</sup> The ratio of D- to L-enantiomeric units affects the degree of crystallinity, melting temperature, and machinability.<sup>10</sup> Therefore, physical properties of the PLA resin can be varied to match numerous performance requirements. Potential advantages of PLA are high mechanical strength, thermoplastic characteristics, biocompatibility, and being derived from renewable resources.<sup>1,4,11</sup> On the other hand, the brittleness, thermal instability, and poor water vapor barrier properties are potential drawbacks for these resins.<sup>1,4,7–10</sup>

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The physical properties of PLA polymers are related to their enantiomeric purity of the lactic acid stereo-*co*-polymer. Depending on the amounts of L-, D-, and *meso*- lactide, high molecular weight PLAs are either amorphous or semicrystalline at room temperature.<sup>7-9</sup> Amorphous PLA polymers are completely brittle below the  $\beta$ -relaxation temperature ( $T_{\beta}$ ) of  $-45^{\circ}\text{C}$ , and near glass transition temperature ( $T_g$ ) of  $58^{\circ}\text{C}$ .<sup>7</sup> PLA undergoes physical aging, thus transitioning from brittle to rubbery state at  $T_g$ .<sup>9</sup> At temperatures of  $110$ – $150^{\circ}\text{C}$ , the polymer transitions from rubbery to viscous state depending on the molecular weight and shear stress.<sup>7-9</sup> The melting temperature is determined from the stereo-chemistry of the PLA polymer. With increasing concentration of mesolactide units, the melting temperature decreases. Pure L- or D-lactide PLA has a melting temperature of  $180^{\circ}\text{C}$ , and the melting temperature increases with increasing molecular weight. Commercially available PLAs exhibit a glass transition temperature around  $50$ – $80^{\circ}\text{C}$ , while the melting temperature ranges from  $130$  to  $180^{\circ}\text{C}$ .<sup>7-12</sup>

Bacterially synthesized poly(hydroxybutyrate) (PHB) are widely studied by researchers and considered a type of PHA's.<sup>3</sup> Commercial use of PHB is limited by low availability, cost of the polymer compared to conventional thermoplastics, narrow processing temperatures due to degradation, and brittleness at room temperature.<sup>3,11,13</sup> For many applications, flexibility of a polymer is required at low temperatures. Incorporation of 3-hydroxyvalerate (HV) during the fermentation process improves these properties and results in lower melting points of the copolymer. This broadens the processing window and decreases brittleness.<sup>2,11</sup> The resulting structure of PHBV copolymer is a nine-carbon numbered chain composed of a randomly distributed copolymer of predominantly 3-hydroxybutyrate (PHB) and 3-hydroxyvalerate (PHV) ending with hydroxyl and carboxyl groups.<sup>1</sup> Therefore, the polymer could be tailored to specific applications that are similar to the conventional thermoplastics.<sup>1</sup> In addition, incorporation of HV content in the backbone helps in improving the melt stability at lower processing temperatures.

Individually, PHBV and PLA polymers have disadvantages when compared to thermoplastics that are currently used. To address high costs and thermal instability, blends of PHBV and PLA were explored as an alternative way of acquiring novel materials with desired properties. Several researchers have studied blends of these polymers as potential applications in packaging to medical sutures. For example, Zhang et al. prepared films by dissolving PLA and PHB in chloroform for film applications, Wang et al. studied the physical properties of coextruded PLA and PHBV polymer blends, and Ferreira

and Duek studied PLA/PHBV blended pins for stabilizing bone fractures.<sup>4,14,15</sup> Additionally, low molecular weight PLA ( $\text{mw} < 18,000$ ) blended with PHB at  $200^{\circ}\text{C}$  resulted in a miscible blend, while PLA and 10% PHB resulted in a new polymer alloy with improved mechanical properties.<sup>15-19</sup> In these studies, low-molecular-weight PLAs (1.8 and 43 kDa) were used, and these researchers focused on two key factors: the miscibility of PLA and PHBV polymers and the potential improvements of the physical properties.<sup>4,14,15,17</sup>

However, current commercial grades of PLA are made by ring-opening polymerization that yields higher molecular weight polymers. Little is known about blends of PHBV with these new commercially available PLAs. Therefore, the aim of this study was to characterize thermal properties of three higher molecular weight PLA resins blended with PHBV. Additionally, the effect of varying PHBV concentrations on thermal properties of the blends was assessed.

## EXPERIMENTAL

### Materials

Commercially available PHBV with 5% HV (T5%) content and a molecular weight of 280 kDa (according to the manufacturer) was obtained from Tianan Biologic Material Co. (Ningbo, China). Ingeo brand semicrystalline PLLA was obtained from Natureworks LLC (Minnetonka, MN) in three different concentrations of D-, L- lactide units. PLA resin 3051D had a weight average molecular weight of 160 kDa and 96% L-lactide to 4% D-lactide units. PLA grade 4042D had a weight average molecular weight of 200 kDa and 92% L-lactide to 8% D-lactide units. The final grade of PLA was 6202D had a weight average molecular weight of 140 kDa with 98% L-lactide to 2% D-lactide units, according to Natureworks LLC.

Blends for each grade of PLA with Tianan 5% PHBV were produced consisting of 20, 30, 40, and 50% PLA. The two polymers were blended using a Daga instrument micro-compounder (Santa Barbara, CA) at  $175^{\circ}\text{C}$  for 10 min with a screw speed of 100 rpm. The blended rods were subjected to thermal characterization. For morphological study, the blended rods were compression-molded into sheets ( $94 \times 94 \times 0.20 \text{ mm}^3$ ) using heating press (Carver Heated Press Model 3851-D Wabash, IN) at  $183^{\circ}\text{C}$ .

### Degradation temperature of blends

Thermogravimetric analysis (TGA) was used to study the weight loss properties as a function of temperature for all the blended rods using a TGA 5000 (TA Instruments New Castle, DE). The blended samples were heated under nitrogen environment

**TABLE I**  
Average Melting Temperatures of T5%/3051D at Four Concentrations Obtained via DSC

T5/3051D	First scan (°C)			Second scan (°C)			Cry. (°C)
	$T_{pm1}$	$T_{pm2}$	$T_{pm3}$	$T_{pm1}$	$T_{pm2}$	Shoulder	
0/100	162	–	–	–	–	–	–
50/50	150 ( $\pm 0.3$ )	–	182 ( $\pm 0.4$ )	149 ( $\pm 0.2$ )	166 ( $\pm 0.4$ )	172 ( $\pm 0.5$ )	122 ( $\pm 0.9$ )
60/40	150 ( $\pm 0.6$ )	168 ( $\pm 0.8$ )	183 ( $\pm 0.3$ )	149 ( $\pm 0.4$ )	166 ( $\pm 0.4$ )	171 ( $\pm 0.1$ )	120 ( $\pm 1.3$ )
70/30	151 ( $\pm 0.2$ )	169 ( $\pm 1.5$ )	184 ( $\pm 0.5$ )	149 ( $\pm 0.6$ )	165 ( $\pm 0.7$ )	171 ( $\pm 0.3$ )	121 ( $\pm 1.6$ )
80/20	152 ( $\pm 0.6$ )	169 ( $\pm 0.3$ )	183 ( $\pm 0.7$ )	148 ( $\pm 0.5$ )	165 ( $\pm 1.3$ )	170 ( $\pm 0.5$ )	116 ( $\pm 0.7$ )
100/0	171 ( $\pm 1.8$ )	–	–	165 ( $\pm 1.0$ )	–	–	–

$T_{pm}$  = peak melting temperature.

from 150 to 500°C with a heating rate of 20 °C/min. Samples were vacuum-dried at 60°C for 24 h prior to any testing. The reported values are averages of at least three samples.

### Phase transition of blends

Differential scanning calorimetry (DSC) was used to determine the glass and melting behaviors. DSC analysis was performed on a TA Instruments Q100 (TA Instruments New Castle, DE). Blended samples were vacuum-dried at 60°C for 24 h prior to any testing. The melting transitions were determined using 5–10 mg samples, and heated from –20 to 200°C with a heating rate of 10 °C/min. The samples were allowed to anneal at 200°C for 5 min to remove the thermal history of the polymers. Subsequently, samples were cooled to –20°C, held for 5 min, and reheated from –20 to 200°C with a heating rate of 10 °C/min. The glass transitions were determined from the second heating with a sample size of 10–20 mg, and a heating rate of 20 °C/min. The reported values are averages of at least three samples.

### Surface morphologies of blends

The surfaces of blends were examined using a Nova Nanosem 400 (FEI Inc. Hillsboro, OR) scanning electron microscope (SEM). The samples (1.0 × 1.0 cm<sup>2</sup>) were coated using Cressington 108 sputter coater (Cressington Scientific Instruments Ltd. Watford,

United Kingdom) with a thin layer of gold–palladium for 3 min. The pictures shown are of the 50/50 compositions of PHBV with three grades of PLA.

## RESULTS AND DISCUSSION

The DSC results of all blends studied are summarized in Tables I–III, and the pure endotherms are shown in Figures 1 and 2. Previous researchers have shown that PHBV is susceptible to thermal degradation, which causes broader endotherm and shift of the highest melting peak to lower temperature in the DSC thermograms.<sup>4,20,21</sup> Based on these findings, comparison between the first and second heating thermograms were studied. To avoid redundancy, more in-depth analysis is provided for PLA 3051D blended with Tianan 5%, since similar transitions were seen with the other PLA's studied. For the first melting thermograms, T5%-3051D at a 50/50 concentration had two melting transitions, while other blend concentrations (60/40, 70/30, and 80/20) had three transitions (Fig. 1 and Table I). The various melting transitions observed for PHBV were attributed to double or multiple melting phenomena, which occurred due to the DSC testing procedure of melting, re-crystallization, and re-melting during heating. However, it is interesting to note that as the concentration of Tianan 5% in the blend increased, an increase in the peak melting area of PHV polymer was observed near 168°C. These results suggest

**TABLE II**  
Average Melting Transitions of T5%/4042D at Four Concentrations Obtained via DSC

T5/4042D	First scan (°C)			Second scan (°C)			Cry. (°C)
	$T_{pm1}$	$T_{pm2}$	$T_{pm3}$	$T_{pm1}$	$T_{pm2}$	Shoulder	
0/100	148 ( $\pm 0.3$ )	–	–	–	–	–	–
50/50	149 ( $\pm 0.1$ )	168 ( $\pm 1.1$ )	183 ( $\pm 0.7$ )	149 ( $\pm 0.2$ )	166 ( $\pm 0.4$ )	171 ( $\pm 0.1$ )	124 ( $\pm 1.5$ )
60/40	151 ( $\pm 0.3$ )	169 ( $\pm 0.8$ )	183 ( $\pm 1.22$ )	149 ( $\pm 0.4$ )	165 ( $\pm 0.5$ )	171 ( $\pm 0.2$ )	124 ( $\pm 2.2$ )
70/30	148 ( $\pm 0.4$ )	169 ( $\pm 0.2$ )	186 ( $\pm 0.4$ )	149 ( $\pm 0.5$ )	166 ( $\pm 0.8$ )	171 ( $\pm 0.6$ )	124 ( $\pm 1.8$ )
80/20	149 ( $\pm 0.8$ )	170 ( $\pm 0.4$ )	183 ( $\pm 1.0$ )	149 ( $\pm 0.3$ )	163 ( $\pm 1.7$ )	170 ( $\pm 0.2$ )	101 ( $\pm 1.3$ )
100/0	171 ( $\pm 1.8$ )	–	–	165 ( $\pm 1.0$ )	–	–	–

$T_{pm}$  = peak melting temperature.

**TABLE III**  
Average Melting Transitions of T5%/6202D at Four Concentrations Obtained via DSC

T5/6202D	First scan (°C)			Second scan (°C)		Cry. (°C)
	$T_{pm1}$	$T_{pm2}$	$T_{pm3}$	$T_{pm1}$	$T_{pm2}$	
0/100	165 ( $\pm 1.2$ )	–	–	–	–	–
50/50	163 ( $\pm 0.1$ )	170 ( $\pm 0.1$ )	183 ( $\pm 0.5$ )	166 ( $\pm 0.4$ )	170 ( $\pm 0.2$ )	104 ( $\pm 1.7$ )
60/40	162 ( $\pm 0.1$ )	–	181 ( $\pm 0.5$ )	157 ( $\pm 1.2$ )	167 ( $\pm 0.3$ )	104 ( $\pm 0.3$ )
70/30	163 ( $\pm 0.8$ )	171 ( $\pm 0.6$ )	183 ( $\pm 1.2$ )	165 ( $\pm 0.5$ )	171 ( $\pm 0.1$ )	98.6 ( $\pm 0.4$ )
80/20	165 ( $\pm 3.8$ )	–	182 ( $\pm 1.3$ )	163 ( $\pm 1.9$ )	170 ( $\pm 0.2$ )	97.6 ( $\pm 2.4$ )
100/0	171 ( $\pm 1.8$ )	–	–	165 ( $\pm 1.0$ )	–	–

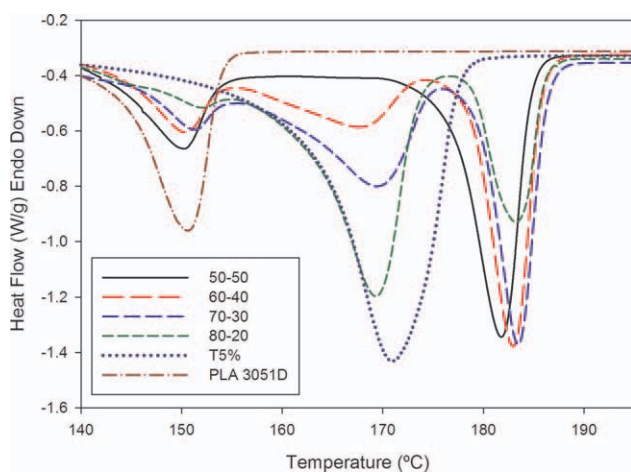
$T_{pm}$  = peak melting temperature

that a higher concentration of PLA is required to achieve a more stable blend.

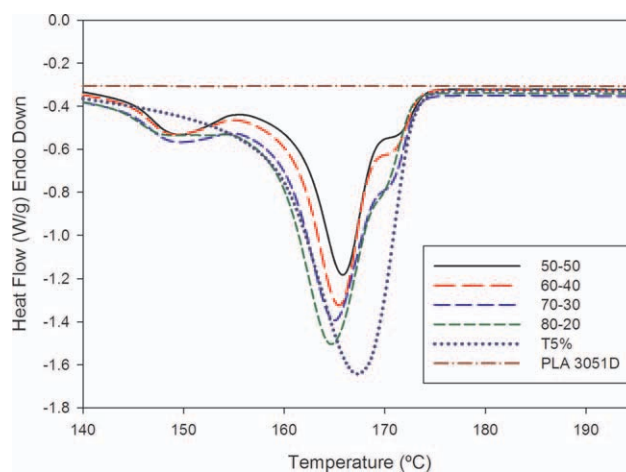
A re-scan (Fig. 2) was performed after annealing the sample for 5 min at 200°C and results showed one large melting peak at 165°C and a residual peak (150°C) from the remaining PLA crystals for all concentrations of T5%-3051D. The large peak (165°C) was similar to the pure Tianan 5% with a shoulder at 171°C, indicating multiple transitions from isothermally crystallized semicrystalline polymer.<sup>22</sup> However, all blends showed two melting peaks suggesting that the polymers melted as individual polymers rather than a homogenous mixture of both polymers (Fig. 2). Multiple melting behaviors of PHBV polyester observed in this study are possibly due to isothermally crystallized polymer. Numerous researchers have reported multiple melting behaviors for PHB, PHBV, and PHA polymers after isothermal crystallization using step-scan DSC.<sup>22–26</sup> Multiple melting peaks are observed due to the following reasons: (1) melting, recrystallization, and re-melting during heating, (2) isodimorphism or polymorphism, which is the presence of multiple crystal modifications, (3) dif-

ferent lamellar thickness, distribution, and morphology, and (4) different molecular weights species.<sup>22,27</sup>

The glass transitions obtained from the second heating scan showed two distinct transitions attributed to PHBV and PLA that are independent of blend compositions when cooling the sample from 200°C (data summarized in Fig. 3). The materials showed relatively no change in the glass transition temperature when compared to the pure Tianan 5% material. On the other hand, the glass transitions for PLA component of the blends decreased by approximately 5°C when compared to pure PLA. Therefore, separate glass and melting transitions suggest that Tianan 5% and PLA 3051D blends are immiscible in their amorphous state. However, it is interesting to note that the glass transition of 50/50 blend was affected more than the other combinations suggesting that some interaction occurred between the polymers at this concentration. Zhang et al. determined that these interactions between PHB and PLA are due to weak bonding between  $\alpha$  methylene groups of PHB to carboxylic group of PLA.<sup>15</sup> Matsuura et al. reported similar types of hydrogen bonding between two similar polymers.<sup>28</sup>

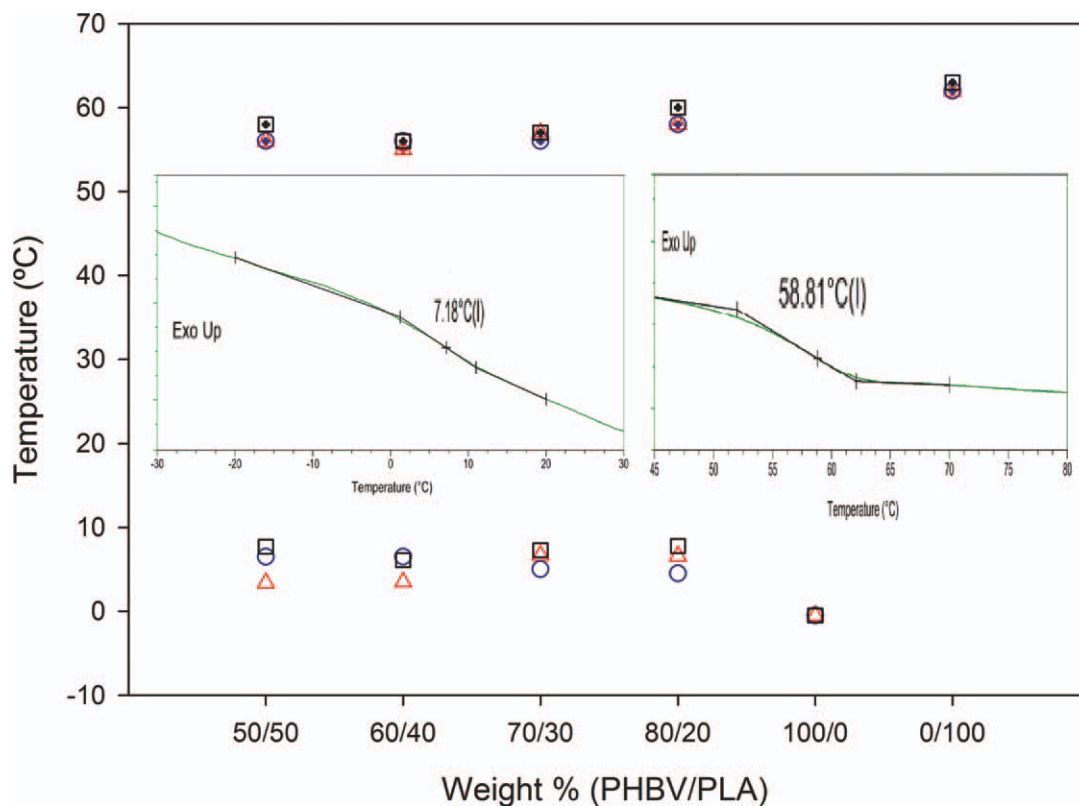


**Figure 1** First melting thermograms of Tianan 5%-PLA 3051D at 10°C/min obtained via DSC. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 2** Second melting thermograms of Tianan 5%-PLA 3051D at 10°C/min obtained via DSC. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





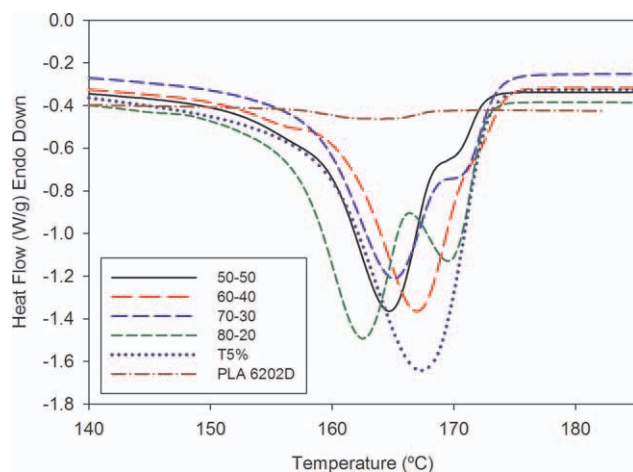
**Figure 3** Average mid-point glass transitions of blends at four concentrations obtained via DSC. The in-lays are Tianan 5%-PLA 6202D 50/50 blend displaying the mid-point  $T_g$ s. Standard deviation of ( $\pm 2.4$ ). (Red triangles = Tianan 5%-PLA 3051D, blue circles = Tianan 5%-PLA 4042D, and black squares = Tianan 5%-PLA 6202D). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

For all concentrations of the Tianan 5% and PLA 4042D blends (T5%-4042D), three distinctive peaks were observed with increasing concentrations of PHBV in the first melting thermograms using DSC (Table II). The melting peaks were observed near 150, 170, and 180°C, as discussed previously for the T5%-3051D and were attributed to PLA, PHV, and PHB respectively. Similar results were observed by Chen et al., for Tianan PHB with 15% HV content.<sup>29</sup> When the first and second heating thermograms were compared, the results showed two unique melts (150 and 165°C) with a shoulder (170°C) for the three concentrations (50/50, 60/40, and 70/30) in the second heating (data not shown). The 80/20 melt showed three distinguishable melts at 149, 163, and 170°C (data not shown). These multiple transitions with a shoulder are associated with the melting of isothermally stable crystals formed during the DSC heating, cooling, and isothermal stages, as discussed previously.<sup>22</sup> With increased PLA addition, a lesser effect on the melt stability of PHBV was observed. Due to the heterogeneous nature of these blends, it was postulated they would be difficult to process in a conventional extruder.

The glass transition of Tianan 5% PHBV blended with PLA 4042D also showed similar results to T5%-

3051D. The PHBV glass transition increased slightly (3°C) approaching the glass transition of PLA, as seen in Figure 3. The glass transition of the PLA component decreased by 8°C as the composition of PLA was decreased from 100 to 20%. Therefore, some compatibility of these polymers was most likely achieved in the amorphous regions.

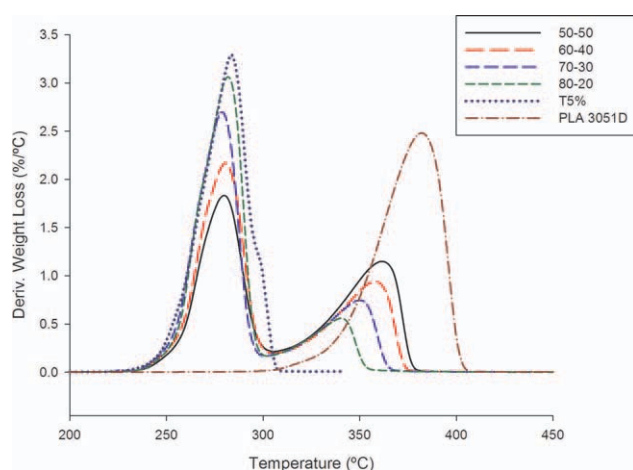
Tianan 5% blended with PLA 6202D (T5%-6202D) polymers showed different melting temperatures at various concentrations of PLA (Table III). The first heating scan for 50/50 and 70/30 concentrations showed three melting temperatures near 163, 170, and 183°C for PLA, PHV, and PHB respectively, as discussed previously for the other blends. However, 60/40 and 80/20 showed two melting transitions near 162 and 181°C for PLA and PHB, respectively. These fewer melting transitions imply greater compatibility of the polymers. On the second heating scan after annealing for 5 min at 200°C, the 60/40 and 80/20 concentrations had separated into two separate peaks compared to a large heterogeneous peak with a shoulder at 165°C for 50/50 and 70/30 concentrations (Fig. 4). The two separate peaks were attributed to isodimorphic characteristic, thus displaying a melting point minimum for PHV with 30 mol % or less.<sup>2</sup> Furthermore, Khanna and Srivastava



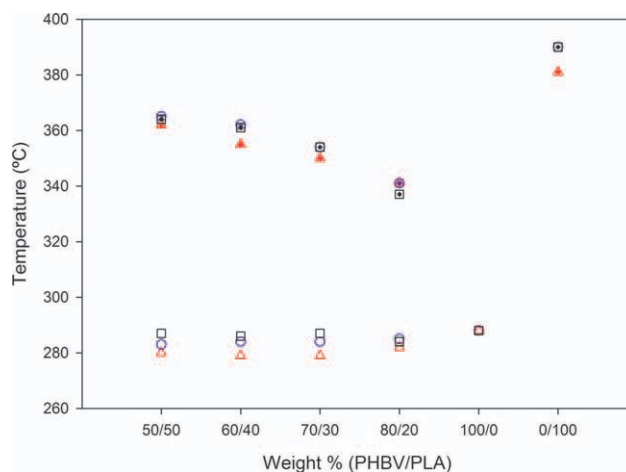
**Figure 4** DSC second melting thermograms of Tianan 5%-PLA 6202D at 10°C/min. (second melting). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

summarized that cocrystallization of the two monomer units occurs in the homo-polymer crystal lattices of PHB, when PHV units are below 40 mol %.<sup>2</sup> These results indicate that the 50/50 blend may lead to best compatibility. The glass transition of T5%-6202D blends showed similar patterns to the other blended polymers (Fig. 3). The first glass transition increased for PHBV portion, while PLA portion of the blends decreased.

TGA curves are shown in Figure 5 for the T5%-3051D blends and summarized for all the blends in Figure 6. The TGA results indicated that PHBV and PLA polymers tend to degrade individually with peak degradation occurring approximately at 280°C and 350°C, respectively. In addition, the peak degradation decreased for PLA with increasing concentration of PHBV. On the other hand, no significant



**Figure 5** TGA thermograms of Tianan 5% and PLA 3051D at four concentrations (20, 30, 40, and 50% PLA). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

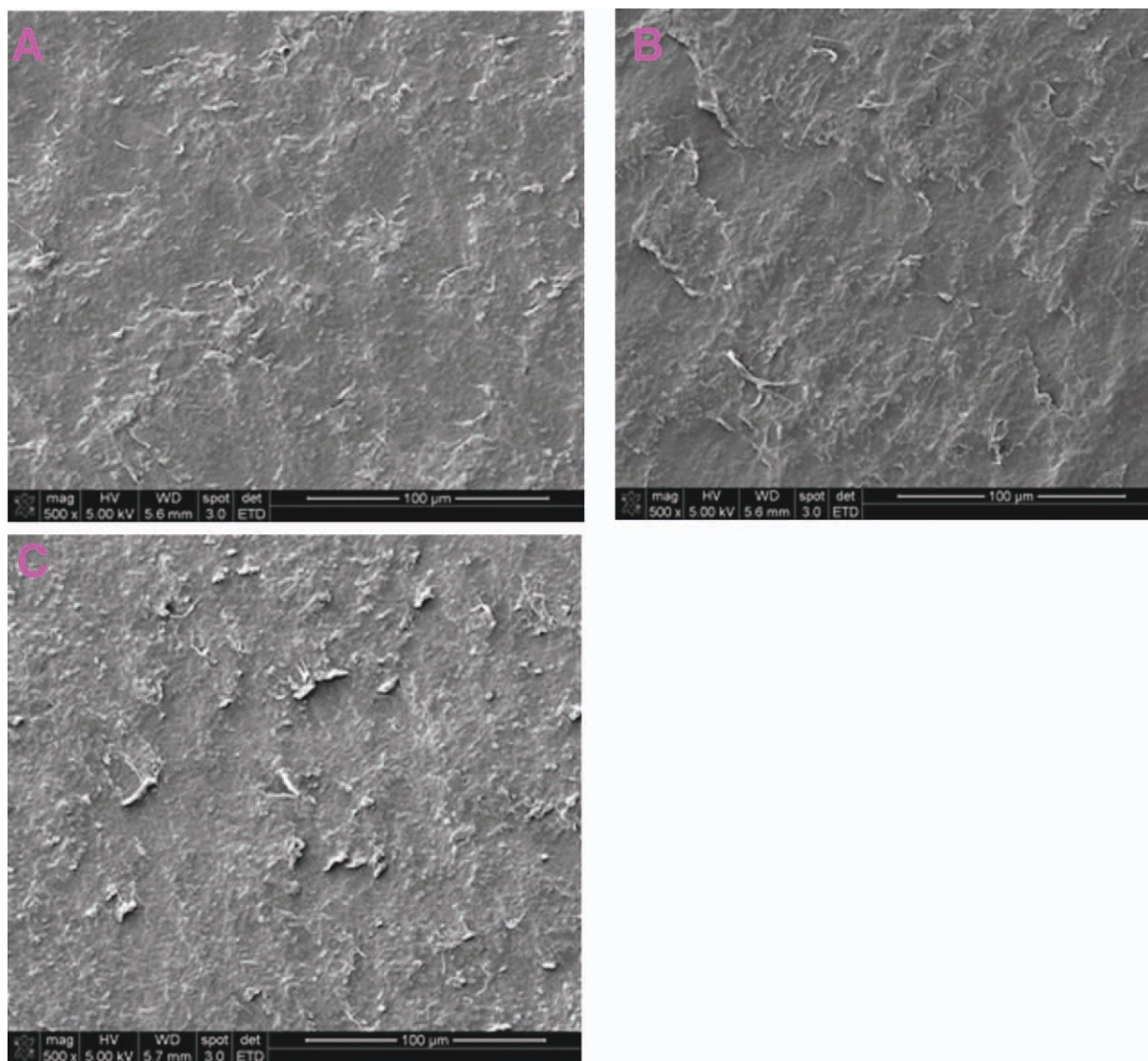


**Figure 6** Average peak thermal degradation temperature of blended polymers with four different concentrations obtained via TGA. Standard deviation ( $\pm 4.6$ ). (Red triangles = Tianan 5%-PLA 3051D, blue circles = Tianan 5%-PLA 4042D, and black squares = Tianan 5%-PLA 6202D). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

changes in the peak degradation temperature were observed for the PHBV polymer. Thus, the TGA data support the DSC analysis that these polymers are mostly immiscible.

The morphological features detected by the SEM are shown in Figure 7(a–c). The SEM examination revealed a nonhomogenous distribution of the PLA polymer into the PHBV matrix. The three different PLA materials showed coarseness around the surface of the PLA/PHBV films. This coarseness was evident by the globular protrusions from the surface of the films, indicating resistance to cracking was low. Under higher magnification, these globular protrusions seemed to have web-like entanglements into the surrounding areas for all PLAs. These entanglements should absorb more energy to fracture and have better toughness, but this was not observed as the films were very sensitive to cracking.

Results for this study are consistent with by Zhang et al., and demonstrate that commercially available PHBV and PLA blends are most compatible for PLA 6202D and higher PLA concentrations for the conditions and materials tested.<sup>15</sup> However, in practical terms, these materials would be difficult to process in an extruder, injection molding, or other processing units. For example, if the higher melting temperature for PHBV is used, then PLA would start to thermally decompose due to its lower melting temperature. According to Hartmann, PLA quickly loses its thermal stability when heated above its melting point.<sup>30</sup> They found significant molecular weight deterioration when PLA was held 10°C above the melting point for significant amounts of time.<sup>30</sup> According to Migliaresi et al., the molecular



**Figure 7** SEM micrographs of fractured surface of Tianan 5% blended with PLAs at 50-50 concentration (a) T5%-3051D; (b) T5%-4042D; (c) T5%-6202D. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

weight deterioration is attributed to PLA's chain splitting.<sup>31</sup> In addition, Aurus et al. summarized PLA's poor thermal stability due to: hydrolysis by trace amounts of water that is catalyzed by hydrolyzed monomer (lactic acids); zipper-like depolymerization, catalyzed by the remaining polymerization catalyst; oxidative random-chain scission; intermolecular transesterification to monomer and oligomeric esters; and intermolecular transesterification resulting in the formation of monomer and oligomeric lactides of low molecular weight.<sup>7</sup>

Yet other researchers have argued that blending these polymers at a higher temperature of 200°C resulted in greater miscibility due to transesterification between PHBV and PLA chains.<sup>20</sup> Ikehara et al. believed that miscible crystalline blends are created from a homogenous melts, where the melting tem-

peratures of the two polymers are very similar. However, immiscible blends are observed when the differences between the melting temperatures of the two polymers are large. For immiscible blends, the polymer with a higher melting point crystallizes first causing the spherulites to fill in the available volume.<sup>15,32</sup> The polymer with a lower melting point is spatially limited inside the spherulites of other polymer.<sup>15,32</sup> When the polymers have similar melting temperatures, both polymers have the ability to cocrystallize.<sup>15,32</sup> Zhang and Ikehara et al. reported that the melting point difference in most miscible crystalline blends is less than 100°C.<sup>32,33</sup> More specifically, the melting point difference between PLA and PHBV in their work was 47°C, which caused simultaneous crystallization.<sup>11,15,32</sup> In this study, the differences between PLA and PHBV melting temperatures were



9 and 23°C for PLA 3051D and 4042D, respectively, yet no simultaneous crystallization occurred, possibly due to the higher molecular weight of the PLAs in this study compared to those in Zhang and Ikehara et al.<sup>32,33</sup>

One of the key variable tested in this study focused on different enantiomeric purity of the lactic acid stereo-isomers. As reported by Yamane and Sasai, the physical properties are greatly affected by the composition of stereo-isomers.<sup>34</sup> For semicrystalline PLAs, which are classified as PLA resins containing more than 93% L-lactide acid, the glass transition temperature has been attributed to the proportion of D-, L-, and mesolactide units present in the PLA polymer system.<sup>7,12,35,36</sup> In addition, the glass transition temperature is higher for PLA containing greater concentration of L-lactide units, compared to D-lactide units. The temperature difference is ascribed to reduced crystallinity in the stereo-isomer polymers, as the presence of both D- and mesolactide units result in imperfections in the crystalline structure.<sup>7</sup> However, the melting temperature is a function of the processing conditions and the stereo-chemistry of the polymer. The melting temperature of the stereo-chemically pure D- or L-lactide is approximately 180°C.<sup>7,34</sup> As reported by Aurus et al., the melting point can be reduced by 50°C with addition of D-lactide units in the polymer structure.<sup>7</sup> In addition, Tsuji and Ikada found that annealing temperature and time affected the melting point. In their study using L-lactide units, they found that melting point and heat of fusion increased with annealing time due to increasing lamellar thickness.<sup>37</sup>

In the present study, the melting temperatures observed were similar to reported values for similar Naturework PLAs with 94 and 98% L-lactide units (140 and 163°C, respectively).<sup>7</sup> The  $T_g$  differed slightly for the same PLA polymers as the reported transitions occurred at 66 and 71°C for 94 and 98% L-lactide units, respectively.<sup>7</sup> The effect of PLA stereo-isomer on PHBV have been studied by other researchers. Owen and Blumm determined that low molecular weight L-lactide acid stereo-isomer (PLLA) diluted the melt and retarded the crystallization rate of PHB.<sup>17</sup> They attributed low crystallization rate to the inability of PHB polymer to diffuse into the growth front for concentration less than 75% of PHB polymer.<sup>17,33</sup> However at greater than 75% PHB concentration in the blend, the PHB polymer is influenced less by PLLA addition as the PHB spherulites grew quickly preventing PLLA-type spherulites.<sup>17</sup> In addition, Zhang et al. determined that the dilution rate of PHB (50% concentrations) in a melt state caused reduced amount of PLLA (50% concentrations) chain segments toward the growing crystals resulting in immiscible blends.<sup>15</sup>

## CONCLUSIONS

The aim of this study was to characterize the thermal properties of commercially available polymers Tianan 5% blended with 0–50% PLA grades 3051D, 4042D, and 6202D at 175°C using a micro-compounder. SEM, melting, glass transition, and decomposition temperatures indicate a significant immiscibility of these various blends. However, promising results were found with the 50/50 blends of T5%-6202D. Future work will focus on adding melt stabilizers by various manufacturers to improve compatibility and processability of this blend.

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