Phase diagrams in blends of poly(3-hydroxybutyric acid) with various aliphatic polyesters

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Abstract. Phase behavior with immiscibility, miscibility, crystalline morphology, and kinetic analysis in blends of poly(3-hydroxybutyric acid) (PHB) with aliphatic polyesters such as poly(butylene adipate) (PBA), poly(ethylene adipate) (PEA), poly(trimethylene adipate) (PTA), or poly(ethylene succinate) (PESu), respectively, were explored mainly using differential scanning calorimeter (DSC) and polarized-light optical microscopy (POM). Immiscibility phase behavior with reversible upper-critical-solution-temperature (UCST) is common in the PHB/polyester blends. The polyester/polyester blend of PHB/PTA is partially miscible with no UCST in melt and amorphous glassy states within a composition range of PTA less than 50 wt%. The miscible crystalline/crystalline blend exhibits ring-banded spherulites at $T_c = 50\sim 100^\circ\text{C}$, with inter-ring spacing dependent on T_c . All immiscible or partially miscible PHB/polyester blends, by contrast, exhibit disrupted ring-banded spherulites or discrete spherical phase domains upon cooling from UCST to crystallization. The blends of PHB with all other aliphatic polyesters, such as PESu, PEA, PBA, etc. are only partially miscible or immiscible with an upper critical solution temperature (UCST) at $180\sim 221^\circ\text{C}$ depending on blend composition. UCST with reversibility was verified.

Keywords: biodegradable polymers, PHB, miscibility, aliphatic polyesters

1. Introduction

Blending of biodegradable poly(3-hydroxybutyric acid) (PHB) or poly(L-lactic acid) (PLLA) with other aliphatic polyesters is one of common approaches to modify the properties of the biodegradable polyesters for various end uses. Blending of PHB or PLLA with other polyesters mostly leads to immiscible mixtures, owing to the fact that the interaction between the biodegradable polyester and other aliphatic polyesters is generally weak or insufficient for leading to a homogeneous mixture at ambient temperatures [1–3]. For example, the blend of poly(ethylene succinate) (PESu) with PLLA was claimed to be immiscible [1]. However, in a later study, it was found that the blend of PESu/PLLA exhibited an upper critical solution temperature (UCST) phase boundary at $\sim 230\sim 250^\circ\text{C}$ [2]. In

addition, Kumagai and Doi [3] reported that PHB was immiscible with poly(ethylene adipate) (PEA) ($M_w = 11\,000\text{ g/mol}$), since the T_g of PEA was independent of the polymer composition after melt-quenched from 200 to -100°C . However, it must be noted that the phase behavior of the PHB/PEA blend (blend of two polyesters) might be temperature-dependent; i.e., phase transition from immiscibility to miscibility at UCST above 200°C could not be ruled out without further investigations. Similarly, the phase behavior of PHB/PEA (or PHB/PESu) could be temperature-dependent, which means that phase behavior of these blends might undergo changes upon heating to some higher temperatures. In addition, the phase behavior in polyester blends may be M_w -dependent as well as temperature dependent. This means that if M_w of either

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of two components is lowered or temperature is changed, the blends of two polyesters may undergo phase transformation with respect to temperature. PLLA or PHB blends with other polyesters might be phase-separated systems at ambient temperature, but actually they may turn into one-phase domain when kept at above a certain temperature range (UCST) or they may become miscible if the molecular weights of either or both components are lowered. Attempts have also been made to blend PHB with PLLA [4–5], however, only partial miscibility in the PLLA/PHB blend was resulted. Preliminary results also indicated that as the molecular weight of PLLA is lowered, PHB/PLLA may become miscible [4, 6]. Phase behavior in polymer blends can be temperature dependent, as revealed in common UCST or lower critical solution temperature (LCST). UCST is normally seen in blends of polymers possessing similar chemical structures or functional groups. Polymer blends that are thermodynamically immiscible at lower temperatures but turn miscible at elevated temperatures (UCST) have been known in some well-studied classical blends of two alike polymers, such as blends of polystyrene (PS) with poly(α -methyl styrene) (P α MS) [7–13]. Most blends involving PHB and PLLA are mixtures of two polymers that interact with each other via either C=O/C=O or C=O/C–O group, which is one type of weak polar-polar interactions. Apparently, the phase behavior in blends of two polymers that do not particularly interact strongly with each other, such as between PHB-polyesters may depend on types of functional groups as well other structural contributions of either of two polymers. Although PHB has been earlier proven to be miscible with poly(ethylene oxide) (PEO) [14–17], it is also known that PHB is not miscible with either poly(propylene oxide) (PPO) or poly(methylene oxide) (POM). Thus, PHB can be miscible with some ether-containing polymers, but not with all of them. POM, PEO, or PPO all have an ether linkage in the main chain, but they differ in main chain structures in terms of varying ratios of the methylene to ether group (–CH₂–/–O–). Such results suggest that interactions between C=O of PHB and C–O group or C=O groups in other polymers are possible, but not all such interactions lead to miscibility. Apparently, structures of the polymers containing these groups (C=O or –O–) are contributing to final

outcome of phase behavior. Similarly, it could be expected that PHB might be miscible with some of the aliphatic polyesters with C=O group in the main chains as long as the structures of the polyesters jointly favor an intermolecular interaction between PHB and the polyesters. It should be noted here that blends with UCST behavior are usually evasive for exact characterization. Blends of PHB/poly(methyl methacrylate) (PMMA) have been claimed by various investigators to be miscibility [18–20], partial miscibility, or utterly immiscibility with two T_g 's [16], while there is only one truth. More interestingly, as the structure of PMMA is replaced with poly(methyl acrylate) (PMA), full miscibility has been reported in PHB/PMA blend [21].

Blend of PHB with poly(1,4-butylene adipate) PBA ($M_w = 14\,000$ g/mol) has been proven to be immiscible by enzymatic degradation observation and its immiscibility is needed to be investigated more to ensure whether the blend is partially or completely immiscible [22]. In continuing on a concurrent investigation on the phase behavior of blends of PLLA with polyesters [23], for comprehensive comparisons, this study further aimed at probing the temperature dependence of phase behavior and phase diagrams of blends systems composed of PHB with a series of aliphatic polyesters of different structures, such as PBA, PEA, poly(trimethylene adipate) (PTA), and PESu, which differ from each other by the CO/CH₂ ratio in the polyester's repeat units. In addition, effects of interactions between PHB and polyesters on the crystalline phase and morphology were analyzed.

2. Experimental

2.1. Materials and procedures

PHB was purchased from Polysciences, Inc. (USA), which has M_w of 500 000 g/mol, PDI = 1.42, $T_g = -4^\circ\text{C}$, and $T_m = 167^\circ\text{C}$. PBA, was obtained from Sigma-Aldrich Inc. (USA), with $M_w = 12\,000$ g/mol, PDI = 1.30, $T_g = -68^\circ\text{C}$, $T_m = 54^\circ\text{C}$, $T_d = 250^\circ\text{C}$. PTA was obtained from Scientific Polymer Products (SP²), Inc. (USA), with $M_w = 8900$ g/mol, PDI = 1.28, $T_g = -60^\circ\text{C}$, $T_m = 38^\circ\text{C}$. PEA was from Sigma-Aldrich Inc. (USA), with $M_w = 10\,000$ g/mol, PDI = 1.30, $T_g = -50^\circ\text{C}$, $T_m = 45^\circ\text{C}$. PESu was from SP² (USA), with $M_w = 10\,000$ g/mol, PDI = 1.9, $T_g = -19^\circ\text{C}$, $T_m = 102^\circ\text{C}$. The molecular weights for most polyesters in this study, with one exception, are

Table 1. Structures, molecular weights, and physical properties of polyesters used in this study

Aliphatic polyesters	Structures	(CH ₂ /CO) ratio
Poly(ethylene succinate), PESu	$\left(\text{O}-(\text{CH}_2)_2-\text{O}-\overset{\text{O}}{\parallel}\text{C}-(\text{CH}_2)_2-\overset{\text{O}}{\parallel}\text{C} \right)_n$	2.0
Poly(ethylene adipate), PEA	$\left(\text{O}-(\text{CH}_2)_2-\text{O}-\overset{\text{O}}{\parallel}\text{C}-(\text{CH}_2)_4-\overset{\text{O}}{\parallel}\text{C} \right)_n$	3.0
Poly(trimethylene adipate), PTA	$\left(\text{O}-(\text{CH}_2)_3-\text{O}-\overset{\text{O}}{\parallel}\text{C}-(\text{CH}_2)_4-\overset{\text{O}}{\parallel}\text{C} \right)_n$	3.5
Poly(1,4-butylene adipate), PBA	$\left(\text{O}-(\text{CH}_2)_4-\text{O}-\overset{\text{O}}{\parallel}\text{C}-(\text{CH}_2)_4-\overset{\text{O}}{\parallel}\text{C} \right)_n$	4.0

high enough to be ~10 000 g/mol. The structures of the polyesters vary in a trend represented by the average ratio of methylene per carbonyl (CH₂/CO) in main chains as shown in Table 1. Except for PESu, T_g 's of these polyesters are between –50 to –70°C, which are quite far away from that of PHB (~0°C).

Blend samples of PHB/polyester were prepared using solvent-mixing, followed by film casting. PHB was purified prior to solvent-mixing. 4 wt% of total polymers in the solvent was dissolved and well stirred in flasks kept just below 40°C. Solvent in polymer mixtures during film casting was first allowed to evaporate by convection under hood for 24 h at 45°C. The blend films were further dried in vacuum at ~45°C for 72 h to drive off residual solvent.

2.2. Apparatus and procedures

Polarized-light optical microscopy (POM)

POM (Optiphot-2-POL, Nikon, Japan) equipped with a charge-coupled device (CCD) digital camera, was used for observing the phase structure of as-cast blends and for monitoring phase transition of blends upon heating. Blend samples were cast as thin films (solvent cast at controlled temperatures and vacuum drying) and placed on a microscope heating stage (Linkam THMS-600 with TP-94 temperature programmer) for OM examination. Recording of temperature dependence of phase transitions in blends was monitored at heating rate of 2°C/min from ambient to phase transition. Growth of spherulites in PHB/polyester blends was observed on CCD digital camera/video. The growth was directly recorded and analyzed via a CCD software package, which allowed the size of the spherulites

in samples be conveniently and automatically measured/recorded at set intervals. The cast-films of PHB/polyester blends with the free surface (i.e. uncovered) upward were first melted on one hot stage at 190°C for 3 min, and then were rapidly transported to the microscopic heating stage pre-set at desired T_c . The purpose was to quickly bring the samples to a designated isothermal crystallization temperature, with minimum temperature lag.

Differential scanning calorimetry (DSC)

Thermal transitions of blends were characterized with a differential scanning calorimeter (DSC-7, Perkin-Elmer Corp., USA) equipped with an intra-cooler for quenching and cooling. Before each T_g measurements, samples were first uniformized in DSC cells (furnace and sample holders) by heating to about 190°C and quenched to sub-ambient (–60°C) before initiating the second scans at 20°C/min. DSC traces were recorded as the second scans. Prior to DSC runs, the temperature and heat of transition of the instrument were calibrated with indium or zinc standards. A continuous nitrogen flow in the DSC sample cell was maintained.

Gel permeation chromatography (GPC)

GPC (Waters, USA) system with styragel® GPC columns (styragel® HR 1, 3, and 4) was used for measuring the M_w and PDI of all samples. Calibration was performed using polystyrene standards.

3. Results and discussion

3.1. Phase and thermal behavior

Blends of PHB with polyesters were preliminarily examined for phase transition upon heating using an OM hot stage. The OM graphs for as-cast

PHB/PTA = 80/20, 50/50 at ambient were initially filled with crystals and small spherulites; however, upon heating the samples to $T = 180^\circ\text{C}$ (above T_m of PHB), the crystals melted and the blends turned into a homogeneous phase at $T = 180^\circ\text{C}$, and they remained homogeneous upon further heating from 180 to $\sim 250^\circ\text{C}$. These results indicate that without the solvent induced PHB/polyester crystals, the blends in the amorphous state were homogeneous. Proving evidence for homogeneity using the T_g criteria will be discussed in later sections. For the PHB/PESu and PHB/PEA blend, however, phase transition is different from the PHB/PTA blend, indicating that the different structure in PESu (from the other polyesters) influences the result of blend's phase behavior.

For details on morphology transitions, Figure 1 shows illustrative OM graphs and scheme plots for as-cast PHB/PESu blend of compositions (25/75, 50/50, 75/25) upon heating from ambient to 176°C for PHB crystal melting, then gradually a maximum 230°C (at $\sim 2^\circ\text{C}/\text{min}$ rate). The as-cast PHB/PESu blend at ambient were initially filled with crystals of small spherulites. Upon heating the samples to $T = 180^\circ\text{C}$ (slightly above $T_m = 167^\circ\text{C}$ for PHB), the crystals melted, revealing apparent two-phase domains in the PHB/PESu blend. That is, by excluding the crystals, the blend was not a homogeneous phase at $T = 180^\circ\text{C}$. However, PHB/PESu blends eventually achieved a homogeneous state

with no visible domains upon further heating to $220\text{--}230^\circ\text{C}$, and remained free of domains up to $\sim 250^\circ\text{C}$ or higher. Further similar experiments of heating using an OM hot stage yielded that the phase transition temperature varied with the blend compositions. For brevity, not all OM results for other blend compositions are shown here. In all, the PHB/PESu blend samples might go through a thermodynamic phase transition from separation to homogeneous phase upon heating, which is known as UCST behavior.

OM characterization on temperature dependence of phase domains in another blend, PHB/PEA, was also performed. Figure 2 shows illustrative OM graphs and scheme plots for as-cast PHB/PEA blend of compositions (25/75, 50/50, 75/25) upon heating from ambient to $\sim 176^\circ\text{C}$ for PHB crystal melting, then gradually to a maximum 230°C (at $\sim 2^\circ\text{C}/\text{min}$ rate). The PHB/PEA blend was found to go through similar phase transition like that in the PHB/PESu blend, except that the transition at which the blend turned from two phases to one phase took place at lower temperatures ($\sim 190^\circ\text{C}$).

Figure 3 summarizes the phase diagrams and UCST for PHB/PESu and PHB/PEA blends of various compositions. The 'clarity point' is defined as the temperature at which the blend samples turn from phase separation (cloudy) into homogeneity with no domains (clear), which apparently depends on the blend compositions. The maximum point is known

Figure 1. OM graphs and schemes for phase domains in PHB/PESu blend of three compositions (25/75, 50/50, 75/25)

Figure 2. OM graphs and scheme plots for phase domains in PHB/PEA blend of three compositions (25/75, 50/50, 75/25)

Figure 3. Phase diagrams showing UCST temperature dependence for PHB/PESu and PHB/PEA blends as a function of composition

as the UCST = 221°C, whose physical meaning is that the blends of all compositions will be one phase at or above this temperature. The asymmetry in the UCST phase curve is expected due to the difference in molecular weight distributions in these two constituents.

3.2. Immiscibility, UCST and reversibility

Rapid quenching of the blend from above UCST was expected to freeze the blends state into a quasi-miscible state. Subsequent DSC scanning on the quench-then-frozen blend samples was performed

to reveal T_g behavior. Figure 4 shows DSC thermograms for PHB/PESu blend of different compositions: (a) 2nd scan after quenching from 190°C (below UCST), and (b) 2nd scan after quenching from 240°C (above UCST). The DSC traces were all 2nd scans on the samples after they were heated to either 190 or 240°C (UCST = 221°C) briefly, then rapid quenched to sub-ambient to freeze the UCST state. DSC traces in Figure 4a apparently show that the blend samples heat to 190°C then quenched are still phase separated; by comparison, all DSC traces in Figure 4b show a single composition-dependent T_g for all compositions in the UCST-quenched blends (heat to 240°C then quenched). Figure 5 shows T_g vs. composition for PHB/PESu blend (by quenching from above UCST). The T_g -composition relationship in exhibits asymmetry in the dependence of T_g with composition. The relationship indicates a homogeneous phase in the blend. However, it must be noted here that the blend was locked into a quasi-homogeneous state as the samples were just freshly quenched from above UCST. With time at temperature for chain mobility, the blend might revert back to phase separation. Figure 6 shows DSC thermograms for PHB/PEA blend of different compositions: (a) 2nd scan after quenching from 180°C, and (b) 2nd scan after quenching from 200°C. For blends either quenched from 180 or 200°C, the 2nd DSC scans on the samples

Figure 4. DSC thermograms for PHB/PESu blend of different compositions: (a) 2nd scan after quenching from 190°C (below UCST), and (b) 2nd scan after quenching from 240°C (above UCST)

Figure 5. T_g vs. composition for PHB/PESu blend (quenched from above UCST)

revealed distinct T_g signal related to PEA, indicating immiscibility of the PHB/PEA blend immediately upon cooling back to below UCST. This DSC result indicates that the PHB/PEA blend could be reverted immediately back to immiscibility upon cooling from UCST state.

Phase reversibility from UCST back to immiscibility at ambient temperature in cooling cycles was further verified for PHB/PESu and PHB/PEA blends. First, the PHB/PESu blend sample was heated to above UCST, then cooled $-2^\circ\text{C}/\text{min}$ from UCST = ~ 240 to 180°C (above T_m but below UCST). When cooled from UCST to 130°C , the blend did not revert immediately back to phase separation. However, this might be due to chain mobility highly

retarded by viscosity. Scientific rigor requires proof that the UCST is a truly thermodynamic process without chemical reactions, such as transesterification, etc. leading to phase changes upon heating. Instead, the UCST-quenched homogeneous blend was dissolved in solvent, re-cast to films, which was then characterized using OM. Apparently, the UCST in the blend could be made to be reversible when viscosity was reduced by solvent. Chemical reactions are not responsible for the phase homogeneity of blend upon heating. If any chemical reactions had been the factors for phase transition into blend homogeneity, then the UCST-quenched blend could not have been reverted back to original phase separation by solvent re-dissolving.

Figure 7 shows OM graphs showing temperature dependence of domains in solvent-recast PHB/PESu or PHB/PEA blend samples that had been heated to UCST: (a) PHB/PESu (50/50), and (b) PHB/PEA (50/50). The OM graphs show that the solvent re-cast samples of UCST-quenched PHB/PESu (50/50) blend were initially filled with phase domains and tiny crystals and small spherulites. Upon re-heating the samples to 180°C (above T_m of PHB), the PHB crystals completely melted, but the phase domains are still apparent. This indicates that the UCST-quenched blend sample was reverted back to phase separation assisted by solvent re-dissolution. The re-cast blend samples upon further heating above T_m eventually achieved again a homogeneous state with no visible domains upon further

Figure 6. DSC thermograms for PHB/PEA blend of different compositions: (a) 2nd scan after quenching from 180°C, and (b) 2nd scan after quenching from 200°C

Figure 7. OM graphs showing reversible UCST temperature dependence of domains in solvent-recast PHB/polyester blends samples that had been heated to UCST: (a) PHB/PESu (50/50), and (b) PHB/PEA (50/50) blend

heating to 230°C, and remained free of domains. In this figure, only the blend composition of 50/50 is used as an example for demonstration; but same results were found for all other blend compositions of PHB/PEA and PHB/PESu.

3.3. Miscibility and crystalline morphology

Thermal analysis was performed to reveal T_g , T_c , and T_m in the PHB/polyester blends of several compositions. Figure 8 shows DSC thermograms for PHB/PTA blend of different compositions. There is only a single, composition-dependent T_g , indicating miscibility. Most miscible binary blends usually follow a relationship as described by the classically known Fox Equation (1):

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (1)$$

Or alternatively, the T_g data can be fitted with the Gordon-Taylor Equation (2) [24]:

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \quad (2)$$

The PHB/PTA blend shows a single T_g for compositions up to PTA = 50 wt%, and the T_g shift with compositions within this range. For PTA > 50 wt%, however, the T_g does not shift so much with composition, although the phase morphology of the blend with PTA > 50 wt% is indeed single-phase. The thermal evidence may still not so strong to indicate miscibility in full range, but partially miscibility up to

Figure 8. (a) DSC thermograms for the PHB/PTA blend of different compositions, and (b) T_g vs. composition curve

Figure 9. POM graphs showing ring-banded morphology in PHB/PTA (50/50) spherulites crystallized at various T_c as indicated

50 wt% of PTA in PHB/PTA blend is plausible. Fitting of the T_g data within the partial miscibility range with the Gordon-Taylor T_g model led to $k = 0.57$. The high value of the G-T k parameter suggests that the miscible PHB/PTA blend has excellent homogeneity. The T_g -vs.-composition relationship shows pretty good fitting with the Fox equation. Miscibility in the amorphous phase of a miscible blend generally influences the crystalline morphology. Figure 9 displays POM graphs showing ring-banded morphology in the miscible PHB/PTA (50/50) blend crystallized at various T_c as indicated. Note that most immiscible crystalline/crystalline polyester/polyester blends exhibit either disrupted or highly distorted ring-banded patterns in crystallized spherulites upon crystallization. Miscibility, on the other hand, tends to retain the patterns of ring

bands in crystallized spherulites in blends. Between $T_c = 50$ to 100°C , the PHB/PTA (50/50) blend crystallizes into ring-banded spherulites with various regularity or inter-ring spacing depending on T_c . The inter-ring spacing and growth rates were measured for the miscible PHB/PTA blend. Figure 10 shows (a) average ring spacing, and (b) spherulite growth rate as functions of T_c for PHB/PTA (50/50) blend. For the PHB/PTA blend, the crystallized spherulites are all ring-banded at $T_c = 50$ to 100°C ; by comparison, the neat PHB crystallizes into ring-banded spherulites at a slightly narrower temperature range. Neat PHB, crystallized at 40°C or lower, exhibits ringless spherulites with distinct Maltese-cross extinction. Only when crystallized at the range of ~ 50 – 90°C , the PHB spherulites are characterized with concentric ring bands of varying inter-

Figure 10. (a) inter-ring spacing, and (b) spherulite growth rate as a function of T_c for PHB/PTA (50/50) blend

Figure 11. (a) DSC thermograms for the PHB/PBA blend of different compositions, and (b) T_g vs. composition relationship indicating a two-phase mixture

ring spacing. When crystallized at 100°C or higher, the spherulites in neat PHB become ringless again. The lower- T_g PTA component widens and lowers the T_c range of forming ring-banded spherulites. For the PHB/PTA blend, the inter-ring spacing of the ring-banded spherulites are the narrowest at $T_c = 70-80^{\circ}\text{C}$, which corresponds to the greatest spherulite growth rate.

Figure 11 shows (a) DSC thermograms for the PHB/PBA blend of different compositions, and (b) T_g vs. composition relationship indicating a two-phase mixture for intermediate blend compositions. The DSC thermograms for the PHB/PBA blend suggest that partial miscibility exists, as indicated by blend

T_g lowering by PBA wt% up to a limit. But phase separation eventually takes place in the blend compositions with PBA contents equal to or greater than 50 wt%. Note also that the apparent T_m of the blend initially shifted with increasing PBA content, but is stabilized at a nearly constant value as the PBA contents approach 50 wt% or greater.

Figure 12 shows OM micrographs of spherulites in PHB/PBA (50/50) blend crystallized at various $T_c = 55-110^{\circ}\text{C}$, within which ring bands in spherulites of the PHB/PBA blend can be seen. The OM graphs show that phase domains are seen along with the ring banded spherulites when cooled and crystallized at T_c . Inset POM graph (right side) for PHB/

Figure 12. OM micrographs of spherulites in PHB/PBA (50/50) blend crystallized at various $T_c = 55\text{--}115^\circ\text{C}$

PBA (50/50) crystallized at $T_c = 60^\circ\text{C}$ shows that ring-banded spherulites are obvious in POM, but phase-separation domains cannot be clearly visible using polarized light as the more distinct crystal structures cover up the less obvious phase-domain images. For this reason, the spherulite crystals and phase separation domains were monitored as functions of temperature using POM and OM respectively. Upon holding at T_c for crystallization of the blend, ring-banded PHB spherulites appeared first, then phase domains of PBA appeared after the crystals are formed. Very likely, the crystals induced phase separation in the blends. Upon heating the blend back to higher temperatures, the ring-banded spherulites first melted at $T = 176^\circ\text{C}$ under OM hot stage, then the domains disappeared upon heating to about $176\text{--}180^\circ\text{C}$ for most blend compositions. Apparently, UCST in the PHB/PBA blend is located at $178\text{--}180^\circ\text{C}$ for all compositions.

4. Conclusions

Phase behavior and miscibility in blends comprising biodegradable PHB and aliphatic polyesters were investigated. Miscibility in partial composition range (PTA contents in blend lower than 50 wt%) is seen in the blends of PHB with an aliphatic polyester, PTA. As the PHB/PTA blend shows a single-phase morphology, no UCST could be observed upon heating. The crystalline/crystalline PHB/PTA blend (50/50), within the miscible range, exhibits ring-banded spherulites at $T_c = 50\text{--}100^\circ\text{C}$, with inter-ring spacing dependent on T_c . All immiscible or partially miscible PHB/polyester blends, by contrast, exhibit disrupted ring-banded

spherulites or discrete spherical phase domains upon cooling from UCST to crystallization. The blends of PHB with all other aliphatic polyesters are partially miscible (with PBA) or immiscible (with PESu, or PEA) with a UCST at $180\text{--}221^\circ\text{C}$ depending on blend composition. UCST with reversibility was verified. Heating to above UCST and quick quenching was proven to preserve the UCST blend into a homogeneous glass state with a single T_g upon DSC scanning, and thermodynamic reversibility of the UCST behavior in the blend was proven by solvent recasting. The chemical structures of the aliphatic polyesters apparently influence the phase behavior. Lower carbonyl density in the aliphatic polyesters leads to less likelihood for miscibility or UCST in the PHB/polyester blends.

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