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Mixtures poly((*R*)-3-hydroxybutyrate) and poly(L-lactic acid) subjected to DSC

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Abstract Blends of bacterial poly((*R*)-3-hydroxybutyrate) (PHB) and poly(L-lactic acid) (PLLA) synthesized by polycondensation of L-lactic acid or by ring-opening polymerization of L-lactide were studied. Miscibility was investigated through both conventional differential scanning calorimetry (DSC) and temperature-modulated DSC (TMDSC). PHB and low-molar mass PLLA were miscible in a whole concentration range, and a single glass transition temperature was observed. On the other hand, PHB/high-molar mass PLLA mixtures phase separate, giving rise to two glass transition temperatures corresponding to PHB and PLLA. A treatment of blends at 190 °C leads to formation of block/multiblock/random copolymers, and blends become miscible.

Keywords Poly((*R*)-3-hydroxybutyrate) · Poly(L-lactic acid) · Poly(L-lactide) · Miscibility · DSC · TMDSC

Introduction

Poly((*R*-)3-hydroxybutyrate) (PHB) has been recognized as a potential environment-friendly substitute for petroleum-based plastic [1]. It is produced by a variety of bacteria. The polymer is linear, highly stereoregular, biodegradable, and biocompatible and, thus, suitable for many biomedical and packaging applications [2, 3]. However, PHB has several shortcomings like brittleness and thermal instability close to its melting point. This causes obstacles for thermoplastic processing technologies. PHB is a highly crystalline polymer, and the growth of cracks within its large spherulites deteriorates its mechanical properties due to secondary crystallization [4].

To overcome these shortcomings of PHB, several approaches have been investigated as follows.

(i) An interesting solution to the problem relies in the biosynthesis of copolymers containing hydroxyalkanoate units other than 3-hydroxybutyrate.
(ii) Chemical modification aims to introduce other structural units into the PHB backbone. The process can be carried out by transesterification reactions of PHB with other polyesters in solution or melt.
(iii) The third approach involves physical modification, i.e., blending of PHB with other polymers using compatibilizers.

Blends of bacterial isotactic PHB and synthetic atactic PHB are miscible when the content of atactic PHB is above 60% [5]. Miscibility of PHB and polyvinyl alcohol depends on the content of residual vinyl acetate structural units [6]. PHB is miscible with poly[(ε-caprolactone)-*co*-(D,L-lactide)] (when the content of the lactic acid structural units is above 41 mol% [7]), and also with poly(oxyethylene) [8] and ethyl cellulose [9].

On the other hand, the blends of PHB and poly(3-hydroxyvalerate) (PHV) include separate phase domains in the melt which consequently crystallize like PHB and PHV types of spherulites [10]. PHB and poly(ε-caprolactone) form immiscible blends [11].

The mixtures of PHB (viscosity-average molar mass, $M_v = 300{,}000$ g mol^{-1}) and poly(D,L-lactide) (number-average molar mass $M_n = 43{,}000$ g mol^{-1}) show on DSC traces two separate glass transition temperatures (T_g) independently of the composition, indicating thus their immiscibility [12].

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On the other hand blends PHB ($M_w = 230{,}000$ g mol^{-1}, $M_n = 87{,}000$ g mol^{-1}) and with more than 50% of poly(D,L-lactic acid) (Resomer R206) were reported miscible based on modulated DSC and DMA [13].

The miscibility of PHB ($M_n = 222{,}000$ g mol^{-1}, weight-average molar mass $M_w = 794{,}000$ g mol^{-1}) with low-molar mass poly(L-lactic acid) (PLLA) ($M_n = 1{,}759$ g mol^{-1}) and high-molar mass PLLA ($M_n = 159{,}400$ g mol^{-1} and $M_w = 416{,}600$ g mol^{-1}) was studied by means of polarization microscopy in Ref. [14]. The former mixtures were miscible whereas the latter showed clearly biphasic separation indicating immiscibility.

We aim to study miscibilities of PHB with both low- and high-molar mass PLLA by DSC or temperature-modulated DSC (TMDSC) in those cases where conventional DSC failed. The effect of sample annealing at 190 °C on DSC traces is also investigated.

Experimental

Materials

Poly((*R*-)3-hydroxybutyrate) (PHB) purchased from Biomer was purified by reprecipitation from a chloroform solution to methanol ($M_v = 285{,}500$ g mol^{-1}). L-lactide from Sigma-Aldrich was purified by a two-fold crystallization from ethyl acetate. L-lactic acid (98%) from Sigma-Aldrich, chloroform p.a. (99.8%) and dichloromethane p.a. (99.9%) from Penta were used as received.

Preparation of poly(L-lactic acid) (PLLA)

Polycondensation of L-lactic acid

L-Lactic acid (310 cm^3) was introduced to a flask equipped with a side arm and a capillary inlet of argon. An air condenser leading to a dry ice/ethanol-cooled receiver was placed on the main arm. The flask was heated by a silicon-oil bath. At defined time periods, the pressure in the system was decreased while the temperature was increased according to Table 1.

After 31 h of polycondensation, the reaction product was dissolved in dichloromethane and precipitated into methanol. The precipitate was dried at room temperature and 20 Pa for 48 h. M_v of poly(L-lactic acid) prepared by polycondensation (PLLA$_{\mathrm{cond}}$) was determined to be 9,200 g mol^{-1}.

Table 1 Reaction conditions of polycondensation of poly(L-lactic acid)

Duration of the given period/h	Temperature/°C	Pressure/Pa
1	100	~67,000
1	120	~60,000
4	150	~50,000
3	150	~10,000
2	150	~270
20	175	~13

Polymerization of L-lactide

Recrystallized L-lactide was polymerized in an ampoule with tin(II) 2-ethylhexanoate (0.1 mol% as related to L-lactide) at 160 °C for 2.5 h. The product of the polymerization was dissolved in dichloromethane and precipitated into methanol. Poly(L-lactic acid) thus obtained (PLLA$_{\mathrm{ROP}}$) was dried to constant mass at room temperature and 20 Pa (for 48 h) [15]. M_v of PLLA$_{\mathrm{ROP}}$ was determined to be 153,100 g mol^{-1}.

Determination of molar mass

The Mark–Houwink constants (cf. Table 2) were used to calculate M_v. Limiting viscosity numbers [η] were calculated using the Huggins equation.

Table 2 Values of the Mark–Houwink constants K and a used for viscometric determination of M_v in chloroform at 30 °C

	$K \times 10^3$/cm^3 g^{-1}	a	Lit.
PHB	11.8	0.78	[16]
PLLA	13.1	0.759	[17]

Preparation of the PHB–PLLA foils

The mixture of PHB and PLLA (0.2 g) having the desired composition was dissolved in 5 cm^3 of chloroform at room temperature (3 h of dissolving). The solution was then poured to a Petri dish (5 cm diameter), the solvent was left to slowly evaporate at room temperature and finally the foils were dried at 20 °C and 20 Pa to constant mass.

DSC

DSC measurements were performed using the DSC module Q100 (TA Instruments) at 50 cm^3 min^{-1} flow rate of nitrogen with sample weight about 5 mg in hermetic aluminum pan:

> *1st run:* −10 to 190 °C, heating rate 10 °C min^{-1}, isothermal at 190 °C (3 min), quenching in liquid nitrogen.
> *2nd run:* (a) −20 to 190 °C, heating rate 10 °C min^{-1} or (b) temperature-modulated DSC (TMDSC) −20 to 190 °C, heating rate 2 °C min^{-1}, modulation ±1 °C/60 s.

Discussion

Poly((*R*)-3-hydroxybutyrate) (PHB) having $M_v = 285{,}500\ \mathrm{g\ mol^{-1}}$ and two types of poly(L-lactic acid) (PLLA) differing in molar mass and in the way of preparation (see "Experimental" section) were used to study the miscibility. "Low-molar mass" PLLA (denoted as $\mathrm{PLLA_{cond}}$) having $M_v = 9{,}200\ \mathrm{g\ mol^{-1}}$ was prepared by polycondensation of L-lactic acid whereas "high-molar mass" PLLA (denoted as $\mathrm{PLLA_{ROP}}$) having $M_v = 153{,}000\ \mathrm{g\ mol^{-1}}$ was prepared by the ring-opening polymerization of L-lactide, initiated by tin(II) 2-ethylhexanoate.

DSC traces recorded at the second heating cycle (after quenching) of the polymer samples used to study the miscibility are presented in Fig. 1. The second run could be affected by the degradation of PHB above its melting point; therefore, annealing time was only 3 min (190 °C). Glass transition temperature (T_g) of the $\mathrm{PLLA_{cond}}$ sample is by 10 °C lower than that of the $\mathrm{PLLA_{ROP}}$ sample. The difference in T_g values reflects not only different molar masses but also the presence of low-molar mass products in $\mathrm{PLLA_{cond}}$ acting as inherent plasticizers lowering T_g. The DSC curves of these two PLLA samples differ also in the position (abscissa) of the melting endotherm which lies for $\mathrm{PLLA_{cond}}$ at a temperature lower by 30 °C than for $\mathrm{PLLA_{ROP}}$; in contrast, the half-width of the melting endotherm of the $\mathrm{PLLA_{cond}}$ is broader due to the difference in molar mass of the measured samples (more than an order of magnitude). The shift of the peaks of cold crystallization (approx. 10 °C) is related to the difference in the flexibility of the chains and their ability to form a crystalline structure. The PHB sample shows $T_g = 6$ °C, exotherm of cold crystallization at ca. 50 °C, and melting temperature (T_m) at 170 °C, these values being similar to those reported in the literature [18].

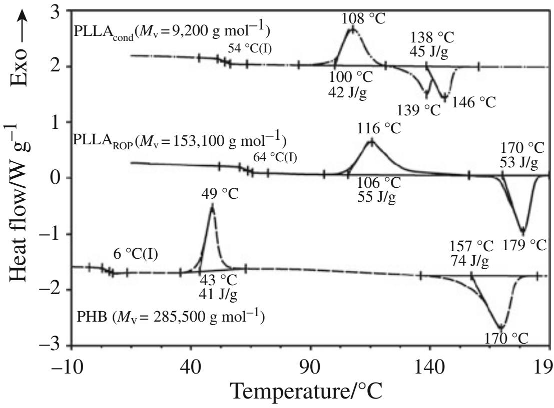


Fig. 1 DSC traces of poly((*R*)-3-hydroxybutyrate) (PHB) and poly(L-lactic acid) (PLLA)—$\mathrm{PLLA_{cond}}$ ($M_v = 9{,}200\ \mathrm{g\ mol^{-1}}$) and $\mathrm{PLLA_{ROP}}$ ($M_v = 153{,}100\ \mathrm{g\ mol^{-1}}$), quenched samples. Heating rate 10 °C $\mathrm{min^{-1}}$, N_2 purge 50 $\mathrm{cm^3\ min^{-1}}$

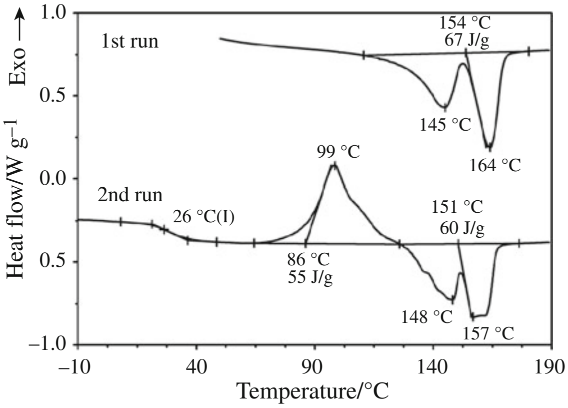


Fig. 2 DSC traces of the 40/60 (wt/wt) $\mathrm{PHB/PLLA_{cond}}$ ($M_v = 9{,}200\ \mathrm{g\ mol^{-1}}$) blend, 1st run (virgin sample), 2nd run (quenched sample). Heating rate 10 °C $\mathrm{min^{-1}}$, N_2 purge 50 $\mathrm{cm^3\ min^{-1}}$

The PHB/PLLA mixtures were prepared from their solutions in chloroform which is a thermodynamically good solvent for both polymers and no equivalent substitute of it can be found for the preparation of polymer mixtures based on PHB. All foils prepared by evaporating the solvent were always homogeneous.

The miscibility of the mixtures was assessed on the basis of T_g values, as measured by DSC. Both polymers contain a high fraction of the crystalline phase and, at the first heating cycle, T_g is difficult to detect. Thus, before the determination of T_g, the sample of the polymer mixture is kept for some time above its melting temperature and then quickly cooled (quenched) to suppress the crystallization of the polymers and get basically amorphous sample. Using this procedure, it was possible to read reliably the T_g values of both homopolymers (Fig. 1) as well as the $\mathrm{PHB/PLLA_{cond}}$ mixtures, as demonstrated in Fig. 2 for the 40/60 mixture.

The $\mathrm{PHB/PLLA_{cond}}$ mixtures

First we have focused on the miscibility of the PHB/$\mathrm{PLLA_{cond}}$ mixtures. Next to the change of the heat capacity of the sample (the inflection assigned to T_g), the peak of the cold crystallization of both components was detected (Fig. 2). A doublet follows, corresponding to the melting endotherm but having a shape different from that recorded at the first heating cycle. This may indicate also changes of the structure of the polymers due to thermal treatment. The presence of a single T_g value lying between the T_g values of both components confirms their miscibility in amorphous regions.

The results of the dependence of T_g on the $\mathrm{PHB/PLLA_{cond}}$ composition of all mixtures prepared are illustrated in Fig. 3. Only a single T_g was indicated for the $\mathrm{PHB/PLLA_{cond}}$ mixtures and its value ranged, depending on the composition of the mixture, between 6 °C (T_g of PHB) and 54 °C (T_g of

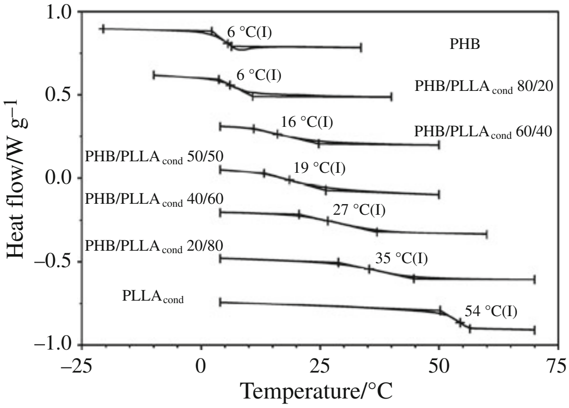


Fig. 3 DSC traces of the PHB and PLLA$_{\text{cond}}$ (M_v = 9,200 g mol^{-1}) and their blends (wt/wt), quenched samples. Heating rate 10 °C min^{-1}, N$_2$ purge 50 cm^3 min^{-1}

PLLA$_{\text{cond}}$). The presence of only one T_g confirms that the amorphous phases of both polymeric components are miscible in the whole concentration range.

The T_g values obtained were compared to those calculated using the Fox equation [19] (cf. Table 3):

$$\frac{1}{T_g} = \frac{w_{\text{PHB}}}{T_{\text{gPHB}}} + \frac{w_{\text{PLLA}}}{T_{\text{gPLLA}}}$$

where w_{PHB}, w_{PLLA}, T_{gPHB}, T_{gPLLA}, and T_g are, respectively, mass fraction of PHB and PLLA, and glass transition temperatures of PHB, PLLA, and the mixture of polymers (in K).

The experimental T_g versus composition dependence does not fit precisely that predicted by the Fox equation. Possible explanation is that, during the quenching of the melt, the PLLA$_{\text{cond}}$ segments crystallize more quickly than the PHB ones (see Fig. 1) and, consequently, the amorphous regions of the mixture contain more amorphous PHB than would correspond to the PHB/PLLA$_{\text{cond}}$ ratio in the original sample.

The maxima of the melting endotherms and melting enthalpies of both components of the mixture are given in Table 3. Both PHB and PLLA$_{\text{cond}}$ form their own crystalline structures (there is a doublet of the melting endotherm in the DSC trace), even though the crystallization of the PHB and PLLA$_{\text{cond}}$ components manifests itself by a single peak of the cold crystallization, as shown in Fig. 2. In the first heating cycle, the melting endotherms of PLLA$_{\text{cond}}$ and PHB are well separated, but the melting enthalpies pertaining to PLLA$_{\text{cond}}$ and PHB cannot be reliably determined. Therefore, also the melting enthalpies of both components are given in Table 3. In the second heating cycle, the separation of the peaks is less pronounced and the melting endotherm of PHB decreases more markedly. The melting enthalpy of the mixture is lower for the second heating cycle than for the first one,

Table 3 DSC of poly((*R*)-3-hydroxybutyrate) (PHB) and poly(L-lactic acid) (PLLA$_{\text{cond}}$) (M_v = 9,200 g mol^{-1}) blends

Mixture	PLLA content/wt%	1st Run (virgin sample)				2nd Run (quenched sample)				T_g/°C	T_g (FOX)/°C	T_{cc}/°C
		T_m (PLLA)/°C	T_m (PHB)/°C	ΔH_m (PLLA)/J g^{-1}	ΔH_m (PHB)/J g^{-1}	T_m (PLLA)/°C	T_m (PHB)/°C	ΔH_m (PLLA)/J g^{-1}	ΔH_m (PHB)/J g^{-1}			
PHB	0	–	173	–	80	–	170	–	74	6	6	49
PHB/PLLA$_{\text{cond}}$ 80/20	20.5	150	167	64		148	165	62		6	15	60
PHB/PLLA$_{\text{cond}}$ 60/40	39.5	145	164	62		144	162	56		15	23	78
PHB/PLLA$_{\text{cond}}$ 50/50	50.1	146	163	58		146	161	56		18	28	81
PHB/PLLA$_{\text{cond}}$ 40/60	60.5	145	164	70		148	157	60		27	33	98
PHB/PLLA$_{\text{cond}}$ 20/80	77.7	144	161	57		147	155	41		38	42	100
PLLA$_{\text{cond}}$	100	148	–	56	–	146	–	41	–	54	54	108

T_m, melting endotherm; ΔH_m, enthalpy of fusion; T_g, glass transition temperature; T_g (FOX), glass transition temperature calculated according to the Fox relation [19]; T_{cc}, exotherm of cold crystallization and this difference increases with increasing content of PLLA$_{cond}$ in the mixture, see Table 3. This is a further evidence of the structural changes of the polymer chains caused by thermal treatment of the mixture, as discussed below.

The PHB/PLLA$_{ROP}$ mixtures

Unlike PLLA$_{cond}$ (T_m = 146 °C), the melting endotherm of PLLA$_{ROP}$ lies at 179 °C and is by 10 °C higher than that of PHB, see Fig. 1. It is seen in Fig. 4 that the melting endotherms of PHB and PLLA$_{ROP}$ in the 40/60 mixture are close to each other (a shoulder is on the trace). In the first heating cycle a peak appears with the melting endotherm at 146 °C and a low melting enthalpy but it disappears in the second heating cycle. As in the previous paragraph, a quenched sample was used to measure T_g of the mixture. Two well-separated cold-crystallization exotherms ($\Delta T \approx 40$ °C) are present in the trace (the first corresponds to PHB, the second to PLLA$_{ROP}$), followed by the melting endotherm. If the PHB/PLLA$_{ROP}$ 40/60 mixture is miscible, then T_g would be approx. 27 °C (see Fig. 3). However, there is no observable change of heat capacity in Fig. 4. In case the polymers are immiscible, the change of heat capacity of (amorphous) PLLA$_{ROP}$ is "hidden" in the exotherm of the cold crystallization of PHB. Hence, the TMDSC technique was used to reliably determine T_g of the mixture under study because it enables the total heat flow to be divided into reversing and nonreversing part, the former being a contribution of the heat capacity.

The TMDSC trace of the PHB/PLLA$_{ROP}$ 40/60 sample, prepared by quenching the melt, at a heating rate of 2 °C min^{-1} and a sinusoidal temperature modulation of ±1 °C/60 s is presented in Fig. 5. The total heat flow shows two cold-crystallization exotherms of the components, that is, PHB and PLLA$_{ROP}$, and a melting endotherm doublet. It follows from the comparison of the cold-crystallization traces of the components in Figs 4 and 5 that the shift toward lower temperatures for TMDSC is caused by a lower heating rate (2 vs. 10 °C min^{-1}). The trace of the nonreversing heat flow shows the same exotherms and the endotherm as that of the total one, as well as the same maxima. The differences in enthalpies are influenced by setting the base-line for the integration. Important information on the properties of the mixtures was obtained from reversing heat flow, the trace of which (Fig. 5) gives two well-separated T_g's related to either component.

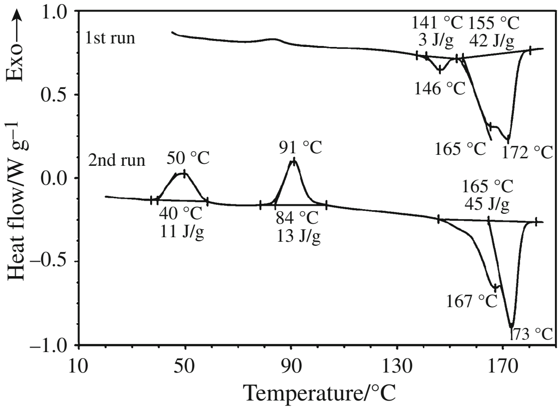


Fig. 4 DSC traces of the 40/60 (wt/wt) PHB/PLLA$_{ROP}$ (M_v = 153,100 g mol^{-1}) blend, 1st run (virgin sample), 2nd run (quenched sample). Heating rate 10 °C min^{-1}, N$_2$ purge 50 cm^3 min^{-1}

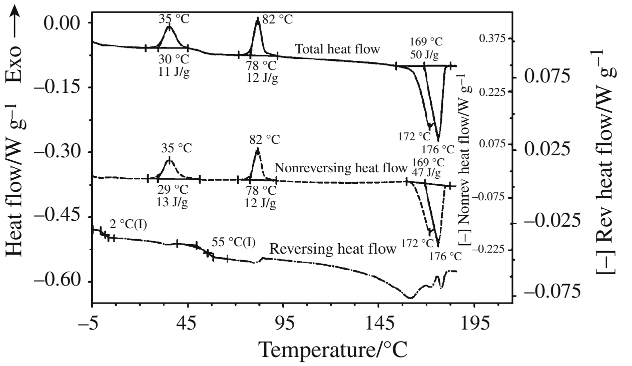


Fig. 5 TMDSC traces of the 40/60 (wt/wt) PHB/PLLA$_{ROP}$ (M_v = 153,100 g mol^{-1}) blend, quenched sample. Heating rate 2 °C min^{-1}, sin modulation ±1 °C/60 s, N$_2$ purge 50 cm^3 min^{-1}

Dependences of the reversing heat flow for all PHB/PLLA$_{ROP}$ mixture compositions under study are shown in Fig. 6 All curves recorded for the mixtures contain two well-identified T_g's of the components, the values of which are close to those of homopolymers and the extent of the heat capacity of the sample reflects their fraction in the mixture. Therefore, the PHB/PLLA$_{ROP}$ mixtures thus prepared are immiscible.

Thermal treatment of the mixtures of poly((R)-3-hydroxybutyrate) and poly(L-lactic acid)

Changes of the position and integrated areas of the endotherms at the second heating cycle, as compared to the first one, suggest not only a change of the crystalline arrangement of the polymer molecules but also a change of the chemical structure of the polymers, as mentioned above for the PHB/PLLA$_{cond}$ mixtures. Miscibility of mixtures can be influenced by a chemical modification, e.g., using transesterification reactions proceeding between the PHB and PLLA chains during the thermal treatment in the melt or in a solution [20]. In addition to the time of heat-treating, the extent of the chemical reactions proceeding in the system can be fundamentally affected by temperature, with regard to the thermal stability of the polymer. It is known that PHB is unstable above melting point. Up to 190 °C

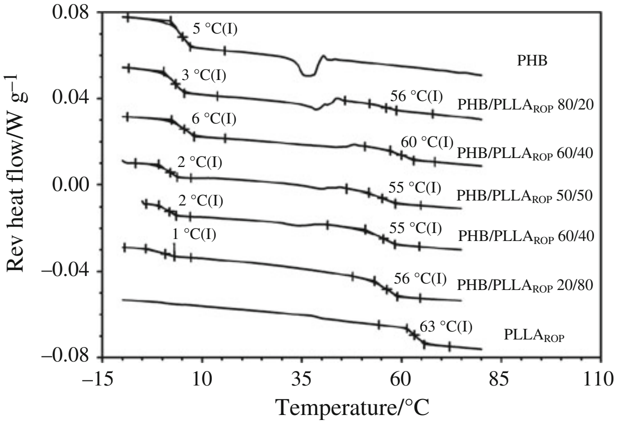
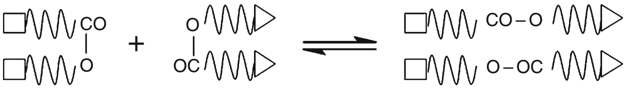


Fig. 6 TMDSC traces (reversing heat flow) of the PHB and PLLA$_{ROP}$ (M_v = 153,100 g mol^{-1}) and their blends (wt/wt), quenched samples. Heating rate 2 °C min^{-1}, sin modulation ±1 °C/60 s, N$_2$ purge 50 cm^3 min^{-1}

there is no significant weight loss (TGA) although changes in molar mass are evidence of degradation of PHB backbone [21]. The decrease in molar mass is about 30% when sample was annealed at 190 °C for 3 min. The more important is random chain scission at ester groups, which results in the formation of carboxyl and vinyl groups. Hence, the temperature of the heat-treating the mixture at 190 °C (i.e., 10 °C above T_m of PLLA$_{ROP}$) represents a compromise between the thermal stability of PHB and a sufficient rate of chemical reactions proceeding between the polymer chains.

The PHB/PLLA$_{ROP}$ mixtures

The PHB/PLLA$_{ROP}$ 50/50 mixture was heat-treated at 190 °C in a gas-tight capsule directly in the measuring cell under nitrogen atmosphere for a chosen time period, then the sample was quenched and finally the curve was recorded in the TMDSC mode (heating rate 2 °C min^{-1}, sin modulation ±1 °C/60 s) (Fig. 7). The change of the chemical structure can be deduced from the changes of T_g values of the components and their post-crystallization. In the trace taken after 3 h of heat-treating at 190 °C, a single T_g appears (16 °C) corresponding to T_g found for the miscible PHB/PLLA$_{cond}$ 50/50 mixture (19 °C, Fig. 3). During the thermal exposition of both polymers, transesterification reactions [20] between the chains could take place (Eq. 1), leading to the formation of block copolymers.



(1)

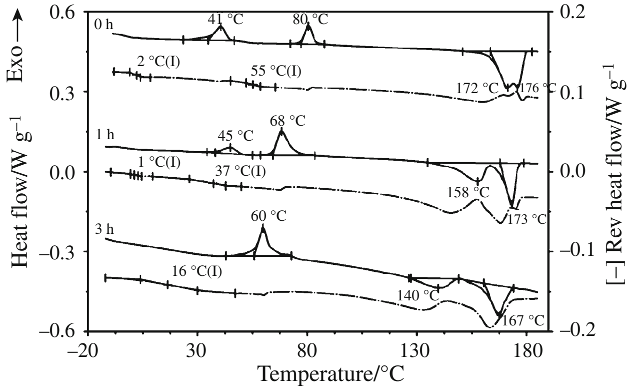


Fig. 7 TMDSC traces (total and reversing heat flow) of the 50/50 (wt/wt) PHB/PLLA$_{ROP}$ (M_v = 153,100 g mol^{-1}) blend (curves parametrized by time of thermal treatment at 190 °C). Heating rate 2 °C min^{-1}, sin modulation ±1 °C/60 s, N$_2$ purge 50 cm^3 min^{-1}

On the other hand, a substantial decrease in molar mass of PHB during thermal treatment [21] contributes to miscibility with PLLA$_{ROP}$.

The PHB/PLLA$_{cond}$ mixtures

The changes in DSC traces of the PHB/PLLA$_{cond}$ 50/50 sample were studied in a similar way as above. The sample was heat-treated at 190 °C for a chosen time period, quenched and heated (DSC, 10 °C min^{-1}, Fig. 8). After 1 h of heat-treating, both melting endotherms shifted to lower values of temperature and the overall melting enthalpy decreased. After 3 h of heat-treating, a single endotherm appeared with temperature lower than T_m of any of both components, and the melting enthalpy dropped to half the value of the original sample. The trace recorded in the second heating cycle contains, after 1 h of heat-treating, two peaks of the cold crystallization, while a single peak after 3 h, even though during this experiment, unlike the measurements of T_g, the samples were not quenched. Again, these changes of melting endotherms and cold-crystallization exotherms relate to the change of the chemical structure of polymers. Similar to the case (a), also here the exchange reactions can be considered to participate in the structural changes of the copolymers (Eq. 1). However, the molar mass of PLLA$_{cond}$ is by an order of magnitude lower than that of PHB or PLLA$_{ROP}$, so that a higher content of end groups (both hydroxy and carboxy) must be taken in account. In this case, alcoholysis of the ester bonds of the chains takes place in the structural changes (Eq. 2):

(2)

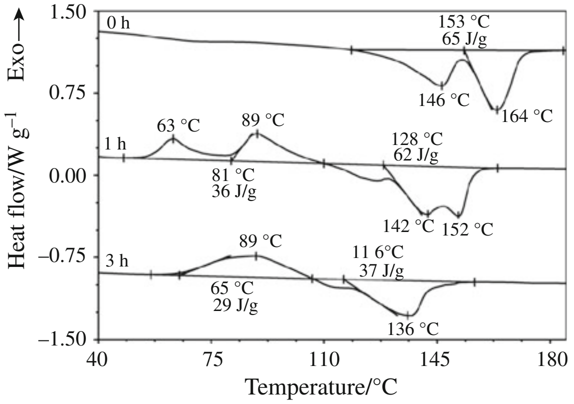
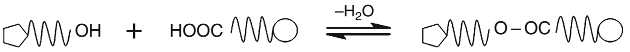


Fig. 8 DSC traces of the 50/50 (wt/wt) PHB/PLLA$_{\mathrm{cond}}$ (M_v = 9,200 g mol^{-1}) blend (curves parametrized by time of thermal treatment at 190 °C). Heating rate 10 °C min^{-1}, N_2 purge 50 cm^3 min^{-1}

Carboxy groups can undergo a condensation with hydroxy groups of PLLA$_{\mathrm{cond}}$ or with those formed by alcoholysis (Eq. 2), the condensation being accompanied by the release of water (Eq. 3). On the other hand, water thus released or formed by the PHB scission [21] may hydrolyze polymer chains (Eq. 4):



(3)

(4)

All these reactions lead in an ideal case to gradual formation of multiblock or even statistical copolymer. This is the reason why only a single melting endotherm and a single T_g appear in the DSC traces, the latter depending on the composition of the mixture.

Conclusions

Miscibility of a commercial sample of poly((*R*)-3-hydroxybutyrate) (PHB) ($M_v = 285{,}500$ g mol^{-1}) with low-molar mass ($M_v = 9{,}200$ g mol^{-1}) or high-molar mass ($M_v = 153{,}100$ g mol^{-1}) poly(L-lactic acid), prepared either by a polycondensation of L-lactic acid or by a ring-opening polymerization of L-lactide, was studied. Mixtures of polymers having various compositions were prepared by casting from chloroform solutions and, after drying, analyzed by DSC.

Miscibility of the mixtures was assessed on the basis of glass transition temperature determination (T_g). To get a reliable T_g value, the sample was heat-treated at 190 °C for 3 min and then quenched in liquid nitrogen. Thus, basically amorphous sample was analyzed. Applicability of the DSC technique for the miscibility studies was influenced by the value of T_g of the homopolymers or the miscible mixture and also by the position of the peaks of cold crystallization of both components.

PHB and low-molar mass PLLA were miscible within the whole concentration range. The change of heat capacity was followed by the peak of cold crystallization, and classical DSC was sufficient for the study of the system. In the case of PHB/high-molar mass PLLA mixtures, the presence of separated peaks of cold crystallization on the DSC trace disallowed T_g to be read. Hence, both miscibility and the phase separation of the components were studied by temperature modulated DSC (TMDSC). It was possible to determine reliably separate T_g's of both components from reversible flow TMDSC which indicates immiscibility of the mixtures.

It followed from the analysis of the DSC traces that thermal treatment applied to both types of mixtures under study led to changes in chemical structure of (co)polymers.

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