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Miscibility and properties of linear poly(L-lactide)/branched poly(L-lactide) copolyester blends

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Abstract

Polymer blends consisting of linear poly(L-lactide) (PLLA) and different proportions of dendritic PLLA-based copolyesters (*hb*-PLLA) characterized by different degrees of branching (DB) were obtained in melt. The solid-state properties of poly(L-lactide)s and their blends were investigated by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), atomic force microscopy (AFM) and stress–strain measurements. DSC and DMA methods proved miscibility of PLLA/*hb*-PLLA blends for the studied composition range. AFM indicated that no phase separation occurs in PLLA/*hb*-PLLA blends and that PLLA and *hb*-PLLA cocrystallize in one single lamellae type. The mechanical characteristics of PLLA/*hb*-PLLA blends deteriorated with an increase of the DB and with changing blend composition. Susceptibility of the blends to biodegradation was studied by measuring the weight loss in two different biodegradation media. PLLA/*hb*-PLLA blends showed more pronounced hydrophilic character and higher susceptibility to biodegradation with an increase in the degree of branching.

Keywords: Dendritic; Polylactide; Blends

1. Introduction

Currently, recycling and biodegradability of polymeric materials are important issues. A central class of biodegradable polymers is aliphatic polyesters, because hydrolytic and/or enzymatic chain cleavage of these materials leads to ω-hydroxyacids, which in most cases are ultimately metabolized.

Poly(L-lactide) (PLLA) is one of the most promising polymers of this class. It can be defined as chemical derivative of L-lactic acid, which is one of the metabolites of the human body and which is widely produced from renewable resources, such as sugar or starch [1]. PLLA has been mainly studied with respect to biomedical applications in surgery, e.g. for surgical sutures [2,3], internal bone fixation [4] and drug delivery systems [5]. In recent years there has been an increasing interest in utilizing PLLA as a bioerodible material in a wide range of commodity applications [6,7]. Progress has also been achieved in polymerization technology. Thus, PLLA is likely to become competitive with lower-priced commodity polymers [8,9]. PLLA is a thermoplastic with a glass transition temperature around 65 °C, a melting point around 175 °C and a degree of crystallization around 70%. PLLA possesses good mechanical properties, with elastic modulus and tensile strength in the range of 3.2–3.7 GPa and 55–60 MPa, respectively [10]. PLLA is a rather brittle and rigid polymer, and compounding of the material with other polymers is frequently employed to improve physical properties or to control biodegradability. PLLA has been blended with a number of different polymers, e.g. poly(3-hydroxy butyrate) [11–13], poly(ε-caprolactone) [14,15], poly(vinyl acetate) [16,17], poly(methyl methacrylate) [18], poly(ethylene oxide) [19,20], polystyrene [21] and polyethylene [22].

In recent years, dendritic polymers, including dendrimers and hyperbranched polymers, have become an important class of polymeric materials that are currently compared with conventional linear thermoplastics in order to evaluate unusual properties. The globular, highly functional structure of dendritic polymers

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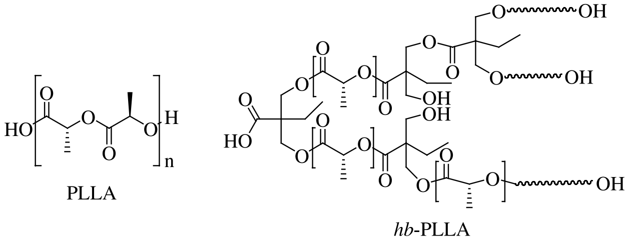


Scheme 1. Structures of linear (PLLA) and branched (*hb*-PLLA) polylactide.

imparts some intriguing properties, such as low melt viscosity and high solubility in various solvents. Numerous potential applications for dendritic polymers have been proposed, e.g. as additives to linear polymers, or in blends [23].

In 1992 Kim and Webster reported blending of hyperbranched polymers with commercial linear polymers [24]. Enhanced miscibility with linear materials would be expected from these dendritic materials and also additional positive effects on the mechanical, rheological and thermal properties of the polymer blends. In recent years various blends between dendritic polyesters and linear polymers have been described, and advantages for processing of the materials due to the dendritic component have been mentioned [25–28].

In all works mentioned, blending of structurally different linear polymers with hyperbranched materials was described. However, for compatibility reasons it is intriguing to study the effect of using a structurally related hyperbranched material for blending with the respective linear chain polymer. In a recent work, we described the synthesis of dendritic aliphatic polylactide-copolyesters based on the combination of ring-opening polymerization and polycondensation of AB_2 monomers [29,30]. By systematic variation of the fraction of the AB_2 comonomer, a series of long-chain branched and hyperbranched copolyesters with different degrees of branching (DB) has been prepared. As expected, the incorporation of branching units affected the thermal properties of the resulting dendritic polylactides. AB_2-fractions exceeding 6 mol% led to the formation of fully amorphous materials.

In this context we summarize the results of blending linear polylactide in different proportions with dendritic polylactides, characterized by different degrees of branching. The structures of both linear and branched PLLA are shown in Scheme 1.

The effect of the dendritic component on both thermal and mechanical properties as well as biodegradability of these blends have been studied and will be reported in the following together with the miscibility behavior of the linear/dendritic polylactide blends.

2. Experimental section

2.1. Materials

Linear poly(L-lactide) (PLLA; $M_w = 110{,}000$ g/mol, $M_w/M_n = 1.3$ by gel permeation chromatography) was purchased from Boehringer Ingelheim and used as received without further purification. Dendritic PLLA-based copolyesters (*hb*-PLLA) were synthesized in our laboratory as described previously (Table 1) [29,30]. In this study, the blends are designated by the percentage of weight of their components. For example, a binary blend containing 90 wt% PLLA and 10 wt% *hb*-PLLA is characterized by the abbreviation 90/10.

Table 1
Dendritic PLLA-copolyesters used for blend preparation

Copolyester	AB_2 (mol%)		DB[a]	GPC	
	Feed	NMR		M_w (g/mol)[b]	M_w/M_n[b]
hb-PLLA2	2	2.2	0.038	21,400	1.75
hb-PLLA5	5	5.1	0.092	10,400	1.36
hb-PLLA10	10	16.8	0.246	2800	2.11

[a] Calculated according to the definition for AB/AB_2 copolymers reported by Hölter et al. [31].

[b] $CHCl_3$ as eluent (PS-standards).

2.2. Blend preparation

Blends of PLLA and *hb*-PLLA were prepared using a Haake Rheocord 90 twin screw extruder. The melt mixing temperature was 190 °C and the screw speed was 60 rpm. All polymers were kept in a vacuum oven at 50 °C for 24 h before processing. The final mixing time was chosen to be 7 min for all blends, which was far after the torque had reached a minimum plateau value. All blends were cooled rapidly in air after the extrusion process. All blends were transformed by compression into 1.5 mm disks for 30 min at 180 °C under vacuum, using a laboratory mechanical press (‘Collin-Plattenpresse’). All samples were held in a vacuum oven at 50 °C for at least 24 h prior to testing. PLLA was processed in the same way as the blends, i.e. it underwent the same mechanical and thermal history.

2.3. Characterization

Thermal properties were measured by differential scanning calorimetry (DSC) using a Perkin–Elmer 7 series thermal analysis system in the range of −50 to 200 °C at heating rates of 36, 25, 16 and 9 K/min. The melting point of indium (156 °C) was used for calibration. The T_g was determined as the midpoint of the heat-capacity increase of the second heating process and T_m as the endothermal peak in the DSC curve of the second heating run.

Dynamic mechanical analysis (DMA) was performed with specimens of $40\times6\times1.5\ \text{mm}^3$ by means of temperature sweeps from 0 to 120 °C for PLLA and from 0 to 85 °C for the blends in a Rheometrics Dynamic Mechanical Analyser RSA II equipped with Dual Cantilever fixture at a frequency of 1 Hz, a strain of 3%, and a scanning rate of 2 K/min. Rheometrics Rhios V4.2.2 PC software was employed to record and analyze the DMA data in real-time.

AFM experiments were carried out with a ‘Nanoscope III’ scanning probe microscope (Digital Instruments) and a Pico Plus scanning probe microscope (molecular imaging) at ambient conditions. The height and phase images were obtained simultaneously while operating the instrument in the tapping mode under ambient conditions. Images were taken at the fundamental resonance frequency of the Si cantilevers which was typically around 170 kHz. Typical scan speeds during recording were 0.3–1 line/s using scan heads with a maximum range of about 20×20 μm^2. The phase images represent the variations of relative phase shifts (i.e. the phase angle of the interacting cantilever relative to the phase angle of the freely oscillating cantilever at the resonance frequency) and are thus able to distinguish materials by their material properties. To visualize the bulk morphology, the samples were microtomed prior to the AFM measurements. Microtomy was performed with an ultramicrotome (Ultracut E, Reichert and Jung). Thin sections of about 30 nm were cut with a Diatome diamond knife at room temperature. The resulting flat surface of the materials was examined by AFM.

Tensile tests were conducted using a Zwick tensiometer (model Z005 (ISO/DP 527)) at 23 °C with a relative humidity of 50%, a power of 5 kN and a mobile clamp speed of 50 mm/min. All samples were kept at the testing temperature for 24 h. Ten samples of each blend were tested and average values reported.

Biodegradation experiments were carried out in vitro at 25 °C for 8 weeks. Each specimen was placed in a vial filled with 0.5 ml bacteria media of pH = 7 containing 0.1 mg *Pseudomonas* sp. or 0.5 ml fungi media of pH = 5.5 containing 0.1 mg *Fusarium* sp. Once per week in the first 4 weeks, the biodegradation media were regenerated with the same media prepared. The last 4 weeks, the media were regenerated with another media, which did not contain any source of carbon, nitrogen, peptone, yeast extract and $NaNO_3$. After 8 weeks of biodegradation, the specimens were withdrawn from the degradation media, washed with distilled water and vacuum-dried at 30 °C. Biodegradation of the polymeric films was monitored by measuring the weight loss.

3. Results and discussion

3.1. Blending

A single composition-dependent T_g is the most used criterion for the miscibility of a polymer blend. To investigate the compatibility of PLLA with the dendritic polylactide copolyesters, all glass transition temperatures were measured by DSC. The DSC thermograms of all PLLA/*hb*-PLLA blends were obtained. The results are summarized in Table 2.

The analysis of the DSC diagrams (Fig. 1) shows that all neat polymers exhibit both T_g and T_m, due to the semicrystalline structure of the materials. The observed decrease of the degree of crystallization of hyperbranched polylactide and finally amorphous morphology at higher degree of branching (DB) (sample *hb*-PLLA10) is explained by the decreasing stability of the crystalline regions and the lowering of the melting point with increasing DB (Table 2).

The presence of T_m and T_g in the DSC diagrams confirms the semicrystalline nature of all blends. However, lowering of both T_m and T_g were observed with an increase of the DB and the content of *hb*-PLLA in the blends. This shows that the branching units do not only affect the crystallizability of the branched materials, but also of their blends with the linear polylactide.

Fig. 1 shows the heat capacity as a function of temperature for PLLA/*hb*-PLLA blends containing 10 and 30 wt% *hb*-PLLA with different DB. Each curve exhibits only one step in heat capacity at the glass transition situated between the T_gs of the neat materials in proportion to the amount of each phase present in the blend, indicating miscibility.

Another method to examine the compatibility of polymer blends is comparison of the measured T_gs with those expected from predictions (Fox equation [32]) based on the thermal characteristics of the neat polymers, as shown below.

$$\frac{1}{T_g} = \frac{w_1}{T_{g_1}} + \frac{w_2}{T_{g_2}} \tag{1}$$

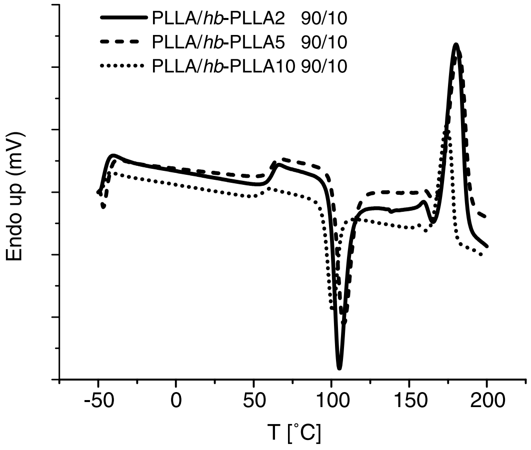
where w_i is the weight fraction and T_{g_i} is the glass transition temperature for each component of the blend.

In some strongly interacting compositions, T_g assumes a maximum with blends composition, most probably due to strong interactions between the two constituent homopolymers [33]. It is important to mention that the positive deviation from the additivity is lower that 2 °C. On the contrary, other studies

Table 2
Thermal characteristics of PLLA/*hb*-PLLA blends for a heating rate of 25 °C/min

Blend composition (wt%)		DB	$T_{g\ DSC}$ (°C)	T_g[a] (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔC_p (J/g °C)	$T_{g\ DMA}$ (°C)
100 (PLLA)	0	0	65.0	–	184.2	–	0.556	73.4
90	10	0.038	62.0	63.6	159.6	180.4	0.575	62.3
70	30	0.038	59.2	61.3	154.6	174.5	0.514	59.7
50	50	0.038	60.8	58.8	176.6	–	0.581	62.0
0	100	0.038	52.9	–	143.0	147.1	0.708	nd[b]
90	10	0.092	61.9	62.5	181.2	–	0.586	62.3
70	30	0.092	57.6	57.8	173.7	–	0.585	57.6
50	50	0.092	51.0	53.4	168.4	–	0.639	47.7
0	100	0.092	45.0	–	142.9	–	0.599	nd[b]
90	10	0.246	56.1	45.4	155.8	174.6	0.587	66.4
70	30	0.246	51.4	28.5	171.6	–	0.688	51.2
50	50	0.246	28.2	20.8	154.5	–	0.629	39.5
0	100	0.246	12.1	–	–	–	0.615	nd[b]

[a] Calculated with Fox equation.
[b] Not determined.



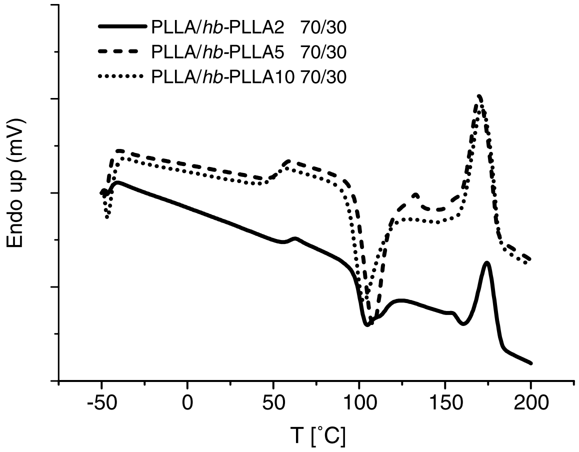


Fig. 1. Typical DSC thermograms of PLLA/*hb*-PLLA blends (heating rate of 25 °C/min).

have demonstrated that positive deviation from the additivity of T_g is not necessarily a blend miscibility criterion [34]. The data in Table 1 show higher T_g values obtained via the Fox equation for the first two series of blends (DB = 0.038 and 0.092). The T_g values for PLLA/*hb*-PLLA10 blends do not exceed the values calculated with the Fox equation.

Generally, PLLA/*hb*-PLLA blends are characterized by one T_m value, but we observed exceptions, which show double melting peaks. This is a common phenomenon for polymers, because melting of the original crystal, subsequent recrystallization, and melting processes during heating are involved.

In addition to DSC, dynamic mechanical analysis is also a very important method to measure T_g for polymers and polymer blends [35]. T_g was evaluated at the point where the mechanical loss (tan δ) from the DMA curves exhibits a maximum. The *hb*-PLLA films obtained by compression-molding were very weak, easily breakable and exhibited virtually no tensile strength. Therefore, DMA measurements were done only for the blends and pure PLLA. Miscibility of the blends is proven by the presence of one single T_g peak in the curves that represents the variation of mechanical loss and the loss modulus (E'') with temperature. evaluation of tan δ and E'' curves showed clearly that the relaxation peak temperature for pure PLLA at 73.4 °C is shifted to lower values with an increase of the DB and with the content of *hb*-PLLA component in the blends, indicating miscibility. Both the intensity and the position of the α-relaxation are considerably affected by the blend composition and degree of crystallization of *hb*-PLLA. Fig. 2 shows that the T_g decreases, as the degree of crystallization decreases and the magnitude of the α-relaxation decreases.

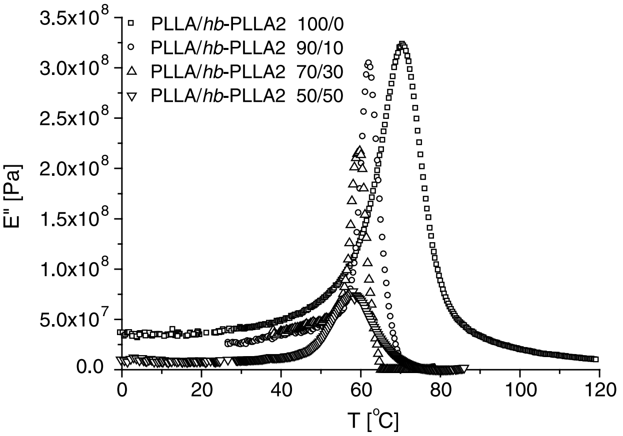


Fig. 2. Loss modulus (E'') vs. temperature of PLLA and PLLA/*hb*-PLLA2 blends measured by DMA.

The reason for the poor mechanical properties of blends is the lack of crystallinity and the absence of entanglements in the branched polyesters. This contributes to the lower storage modulus obtained for the PLLA/*hb*-PLLA blends, compared with the value for the linear PLLA. The characteristic drop in the E' value is due to more abrupt glass transition effects for the blends that contain *hb*-PLLA with higher DB. The DMA measurements do not show E' modulus traces close to that of pure PLLA, which confirms that the E' modulus is also strongly influenced by the fraction of branched copolyester (Fig. 3).

DMA measurements demonstrate clearly that in order to obtain a blend for specific applications, the modulus of the blends can be controlled by mixing the polymers in the desired proportions. The changes of the mechanical properties of the

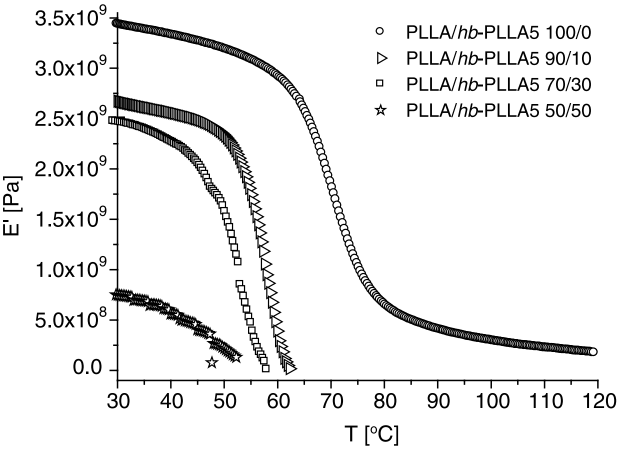


Fig. 3. Storage modulus E' vs. temperature of PLLA and PLLA/*hb*-PLLA5 blends measured by DMA.

blends are correlated with a variation of the thermal properties, degree of branching and composition.

The miscibility of the blends was also studied via AFM measurements. Melting of the blends leads to homogenous melts, i.e. no phase separation in the molten state is observed in all cases studied. Fig. 4(a) exemplarily shows a quenched melt of PLLA/*hb*-PLLA10-50/50. Quenching was performed fast enough to avoid crystallization. After quenching, the AFM measurements were performed at room temperature; e.g. above the T_g of *hb*-PLLA10, and below the T_g of PLLA. Therefore, very good contrast between the respective phases would be observed by AFM, if a phase separation occurred. The absence of a segregated morphology evidences the melt miscibility of the *hb*-PLLA10 with PLLA. Fig. 4(d) shows a PLLA/*hb*-PLLA10 50/50 blend after crystallization. The sample was microtomed to observe the bulk structure. In contrast to the quenched sample, homogeneously distributed lamellae could be observed, with a high contrast between crystalline lamellae and amorphous regions in-between the lamellae. Pure PLLA crystallized and measured under the same conditions shows only a very weak phase contrast between crystalline and amorphous regions, due to similar stiffness of crystalline PLLA and amorphous glassy PLLA. The high contrast observed in the blend indicates that *hb*-PLLA10 is enriched in-between the PLLA lamellae. The crystallization process leads to phase separation of the components, and the amorphous *hb*-PLLA10 is arranged regularly between the crystallized lamellae of the PLLA. Additionally, no extended *hb*-PLLA10 phases were observed in the crystallized sample. This supports again the melt-miscibility of *hb*-PLLA10 and PLLA.

Fig. 4(b) and (c) shows the crystalline morphology of 4b: PLLA and 4c: PLLA/hb-PLLA5 50/50. All AFM measurements were performed on surfaces crystallized in vacuum. In contrast to the sectioned sample (4d), the lamellae show mainly a flat-on orientation. In both samples broad lamellae were observed. As a result of a reduced crystallization rate the lamella observed for the blend PLLA/hb-PLLA5 50/50 are more ordered than the lamellae of PLLA. Within the blend only one type of lamellae was observed. This means that PLLA and hb-PLLA5 cocrystallized. This is in agreement with the observation of a single melting point and a single spherulite growth rate.

The miscibility of the PLLA/*hb*-PLLA blends confirmed by DSC, DMA and AFM methods could be the result of the similar chemical structure of PLLA and *hb*-PLLA. In this case, this factor is more important in determining the phase behavior of the studied blends than the architecture of the polymeric components.

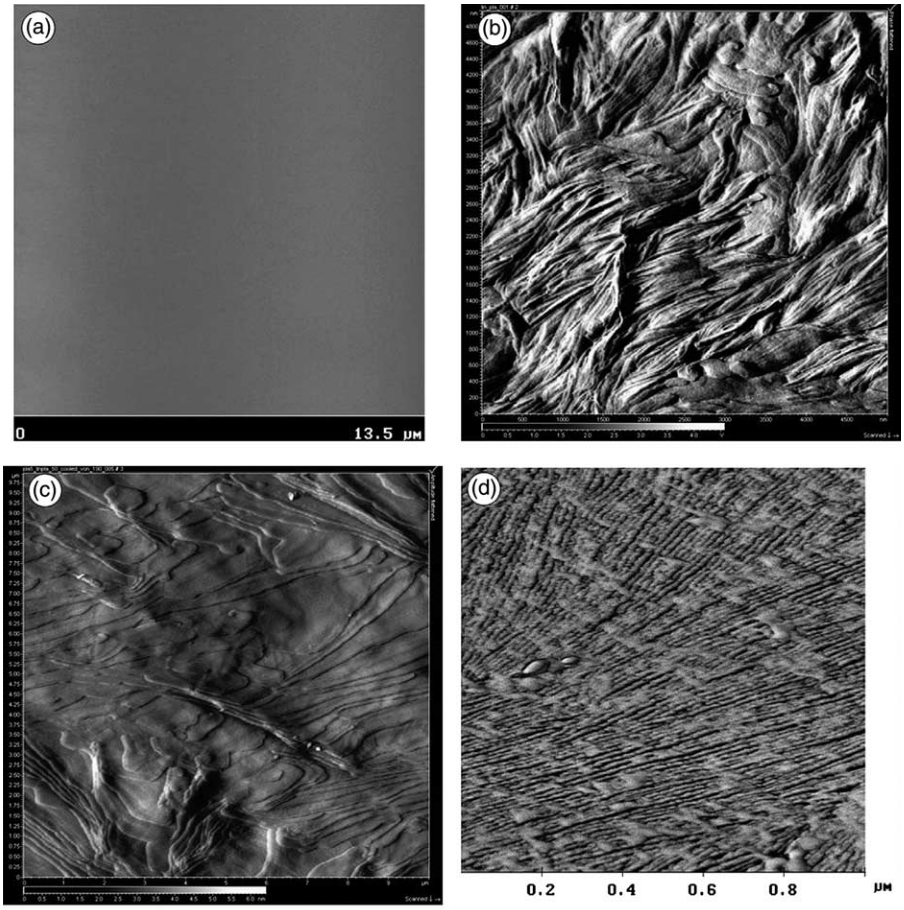


Fig. 4. AFM phase images for (a) a quenched melt of PLLA/*hb*-PLLA10 50/50 and crystallized samples of (b) PLLA, (c) PLLA/*hb*-PLLA5 50/50 and (d) PLLA/*hb*-PLLA10 50/50.

Table 3
Mechanical Properties of PLLA/*hb*-PLLA Blends

Blend composition (wt%)		DB	Tensile strength, σ_F (MPa)	Young's modulus, E (MPa)	Elongation at break, ε_F (%)
100 (PLLA)	0	–	50.8	2397	5.4
90	10	0.038	41.1	1955	3.3
70	30	0.038	25.5	1796	1.7
50	50	0.038	–[a]	974	–[a]
90	10	0.092	25.8	1258	5.0
70	30	0.092	9.3	1144	0.7
50	50	0.092	5.1	544	0.6
90	10	0.246	11.6	1073	0.9
70	30	0.246	5.4	920	0.9
50	50	0.246	–[a]	654	–[a]

[a] Values situated below the measuring limits of the instrument.

From a practical point of view, the effect of the dendritic polymers on the mechanical properties of the polymer blends is of considerable interest. Analyzing the stress–strain curves (not shown here) of the neat polymer PLLA and PLLA/*hb*-PLLA2 and PLLA/*hb*-PLLA5 blends that contain 10% it was obvious that they behave like tough thermoplastics that do not exhibit a yield point. All of the PLLA/*hb*-PLLA compositions behave like rigid materials and exhibit total deformation at stress, which is shown in the complete break of the test specimens.

As expected, the results presented in Table 3 show that PLLA/*hb*-PLLA blends are characterized by lower values of the main mechanical characteristics studied (tensile strength, Young's modulus, elongation at break) in comparison with the linear polylactide. It was evident that an increase of *hb*-PLLA proportion in the blends and higher DBs lead to a decrease of mechanical characteristics.

3.2. Biodegradation

It is well known that PLLA is an intrinsically semicrystalline compound, which degrades hydrolytically very slowly [36–38]. The biodegradation rate of PLLA is strongly influenced by its morphology and crystallinity. Both these properties can easily be modified by blending PLLA with polymers that yield materials with large differences in T_g and/or crystallinity. Some preliminary results on the biodegradation behavior of PLLA/*hb*-PLLA blends are reported in the following.

The effect of microorganisms on degradation of PLLA and PLLA/*hb*-PLLA blends was compared by using fungi and bacteria as media of biodegradation. Analyzing the results obtained after 60 days of biodegradation for PLLA, *hb*-PLLA samples and their blends, in *Pseudomonas* sp. and *Fusarium* sp. media, a significant increase of the weight loss for the compositions with higher than 30% *hb*-PLLA content was found (Fig. 5). For the blends containing *hb*-PLLA10 with M_w of 2800 g/mol, the weight loss could be also the result of dissolution of the low molecular weight hyperbranched material. Generally, the biodegradation occurs first in the lower crystalline regions because of the higher accessibility of the microorganisms due to the higher mobility of the chains. This is the reason, why *hb*-PLLA, which is less crystalline than PLLA is more prone to microbial attack. In addition to the effect of molecular weight on the biodegradation rate, the more hydrophilic nature of the branched structures promotes swelling in the biodegradation media and thereby enhances the degradation process. *Pseudomonas* sp. showed the strongest activity on accelerating the degradation of PLLA/*hb*-PLLA blends compared with the *Fusarium* sp. media (Fig. 5).

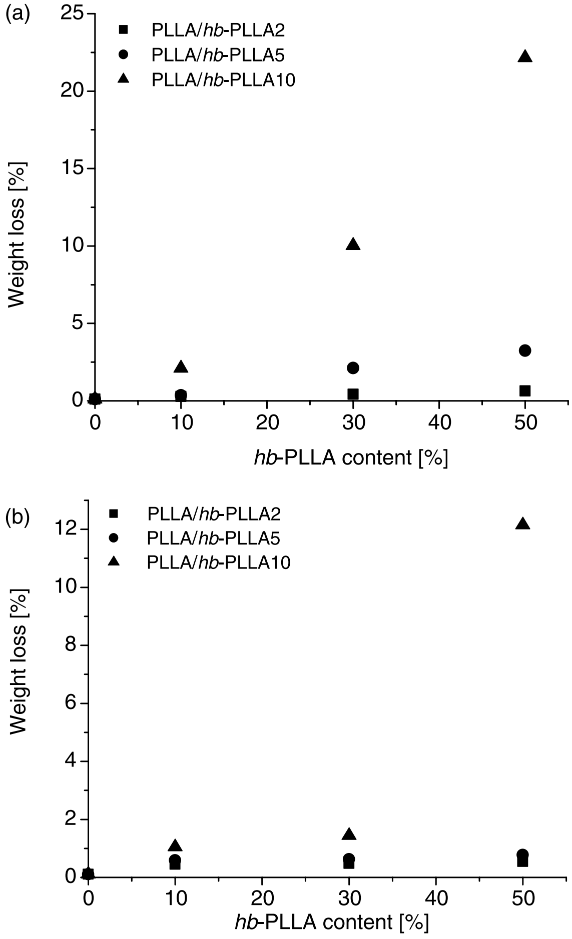


Fig. 5. Plot of the weight loss of PLLA/*hb*-PLLA blends after degradation in (a) *Pseudomonas* sp. and (b) *Fusarium* sp. media.

Blending PLLA with branched polylactide can enhance the range of application of PLLA in the biomedical field. For example, modification of polymer–polymer phase behavior during the biodegradation process could be a way to allow the manipulation of drug release properties. Other possible applications of biodegradable polylactide blends would be in food packaging and contaminated hospital waste, which are not suitable for collecting and recycling.

4. Summary and conclusions

The aim of this study was to investigate the miscibility and some properties of PLLA/*hb*-PLLA blends. The miscibility was studied using DSC, DMA and AFM. All methods employed evidenced completely miscible blends for the analyzed composition range. A decrease of the mechanical characteristics with an increase of the degree of branching and the proportion of the dendritic component in PLLA/*hb*-PLLA blends was observed. Biodegradable blends were obtained, the rate of biodegradation being mainly controlled by the degree of crystallization and the molecular weight of the blend components.

In conclusion, controllable biodegradability in combination with favorable mechanical properties and miscibility may extend the application potential of PLLA blends in the biomedical field.

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