Stress–Strain Behavior of Blends of Bacterial Polyhydroxybutyrate

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ABSTRACT: A series of blends of bacterial poly(R-hydroxybutyrate) (PHB), with different miscible amorphous components, were prepared. The molecular mass of the amorphous components was varied from $M_n \approx 600$ to 200,000 g/mol. Several factors were found to influence the stress–strain behavior of PHB blends: the glass-transition temperature, the average molecular mass of amorphous phase, the content of PHB in the blend, the crystallinity, and the drawing temperature. It was found that a high extension ratio at rupture $\lambda_R > 3$ is obtained only if the PHB content is less than 60% (crystallinity $X_c < 0.4$), although this holds only for blends of bacterial PHB with a high molecular mass ($M_n > 30,000$) amorphous component. The lowering of glass-transition temperature by the addition of low molecular mass additives (plasticizers) deteriorates the tensile properties. Measurements at elevated temperatures of ductile blends yielded a marked decrease of both stress at rupture σ_R and extension ratio at rupture λ_R. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 2528–2537, 2004

Key words: bacterial poly(R-hydroxybutyrate); stress; strain; blends; elongation at break

INTRODUCTION

Poly-(R)-3-hydroxybutyrate (R-PHB) is a bacterial polyester[1] with the potential to reduce the use of commercial polymers, based on fossil carbon sources, in the future. R-PHB is based on naturally occurring and cheap raw materials, and it has several advantageous properties, as well as biocompatibility and biodegradability. However, the pure bacterially produced R-PHB has two main drawbacks:

1. A high melting point, 173°C, and thermal degradation that begins around 200°C, thus leaving only a narrow temperature window for thermoplastic processing.[2]
2. Rather inelastic behavior and significant embrittlement during storage at room temperature.

The mechanical ageing of PHB has been studied by using a number of testing techniques. The tensile modulus has been shown to increase linearly with the logarithm of ageing time, from about 1.5 GPa of the freshly molded material up to 3.5 GPa,[3] whereas the impact strength decreases concomitantly with a reduction of the magnitude of tan δ loss peak[3,4] and a very low maximum extension ratio λ_R of only 1.02.

Several authors, who studied the embrittlement of PHB,[5–10] attributed this ageing behavior to the following phenomena:

- Large volume-filling spherulites from few nuclei because of the high purity of PHB.[5,6]
- Progressive crystallization process occurring upon storage of the material, where a crystallinity X_c of about 60% is reached after storage.[5]
- The glass transition of PHB ($0 \pm 5°C$, by DSC, and 25°C at 1 Hz by dynamic mechanical analysis[8]), which is close to the testing temperature.
- Secondary crystallization, in which the amorphous phase between the crystals becomes constrained.[3,4,7,8,9,10]

Several efforts have been carried out to improve the mechanical properties of PHB, such as addition of nucleating agents,[11] which can reduce the size of the spherulitic crystals. However, it was reported[12] that the maximum extension ratio to break was only slightly increased (λ_R values from 1.01 to 1.05) by nucleating agents.

Other attempts to improve the mechanical properties include the addition of plasticizers such as citrate

esters,[13] tributyrine,[14] or the annealing of PHB at higher temperatures (110°C for instance).[4]

Another approach to better materials was to produce new bacterial copolymers, such as poly(hydroxybutyrate-*co*-hydroxyvalerate),[15] although such production is very expensive, and the crystallization requires longer times than those for pure PHB,[16] which leads to a longer cycle time for injection molding. Other authors tried to synthesize block copoly(ester-urethanes).[17,18]

The most economical method, however, has proved to be blending with other polymers.[19]

Properties of immiscible blends with heterogeneous microstructure

The modulus, stress, and elongation at rupture for PHB/rubber blends were previously studied,[20] but for an immiscible blend of 80% PHB with 20% ethylene propylene rubber-*grafted*-sodium acrylate (EPR-*g*-SA) the maximum extension ratio λ_R was only 1.07. For blends of PHB/polybutylacrylate (PBA),[21] the Young modulus and tensile strength decrease linearly with increasing weight fraction of PBA in the film. Similarly, for PHB/polycaprolactone (PCL) blend film[21] these properties decreased with an increasing weight fraction of PCL and reached a minimum value at around 50 wt % of the PCL component. The maximum extension ratios λ_R for PHB/PCL and PHB/PBA are 1.11 and 1.07, respectively. On the other hand, the PHB film becomes flexible and tough on blending with a block copolymer [*R,S*-PHB-*b*-ethylene glycol (EG)], the extension ratio λ_R increases from 1.05 to 1.9 as the fraction of the block copolymer component increases from 0 to 50 wt %.[22]

Properties of miscible blends

For miscible blends of PHB with atactic *R,S*-PHB[23,24] it was found that the extension ratio λ_R increases from 1.05 to 6 as the content of *R,S*-PHB increases from 0 to 76%. Recently, a miscible blend of PHB with polyvinylacetate (PVAC) and some plasticizer was investigated and an elongation at break $\lambda_R = 5$ was determined.[25]

From an overview of published studies, we have to conclude that the correlation between the tensile properties of tough blends of PHB and the thermal properties of these blends are not known satisfactorily from the literature. It is difficult to compare the tensile properties of PHB blends reported by different authors because some studies measured specimens that were cast from solution[23,24] and others measured injection-molded films.[20,21,25] Moreover, crystallization conditions were generally not the same. Tensile testing of PHB blends at elevated temperature, to our knowledge, has not been reported in the literature.

In this article we present the results of investigations on blends of PHB with miscible amorphous polymers that are able to improve the tensile properties of PHB. We systematically studied those factors that have a substantial influence on the tensile properties of the PHB blend, such as molecular mass, glass-transition temperature, tensile test temperature, and composition of the blend, and the interrelationship between the tensile test behavior and the structural properties, such as percentage of crystallinity for example.

EXPERIMENTAL

Materials

Pure bacterial isotactic poly-(*R*)-hydroxybutyrate (PHB) was kindly supplied by Dr. Haenggi, Biomer Company, Darmstadt, Germany. The PHB content is given as >98%, the content of polyhydroxyvalerate (PHV) < 1%, and the remaining cell membrane and membrane lipids content about 1%. PHB was obtained as a powder and used as received without further purification.

The oligomers, atactic *R,S*-PHB-OH (abbreviated as G2670 and G610, depending on the molar mass), were prepared by transesterification of ethyl hydroxybutyrate with butylene glycol in the presence of dibutyltinoxide as catalyst. For details of this method see Saad et al.[26] All of the oligomers were dissolved in chloroform followed by precipitation with excess hexane. The hexane layer was decanted off, and the oligomers were washed several times with hexane to remove the residual unreacted monomer, as well as traces of the catalyst. Finally, the oligomer was dried under vacuum at 60°C for 48 h. The thermal properties (glass transition, melting behavior) of these oligomers and their blends with PHB are described in another publication.[27]

The material abbreviated as L30,000, is an atactic synthetic polyhydroxybutyrate [P(*R,S*-3HB)]. It was prepared by ring-opening polymerization of racemic β-butyrolactone at 100°C for 24 h, in the presence of dibutyltinoxide as catalyst, using a previously described method.[28] This atactic *R,S*-PHB has a tacticity index of 0.4 from ^{13}C-NMR. For practical application, it can be considered as amorphous. It crystallizes only after a long time (~ 2 months) at room temperature. In this case, we found a melting peak with T_m in the range of 50–60°C but only in the first scan, similar to the melting point previously found by Kricheldorf and Eggerstedt.[28] The glass-transition temperature T_g of L30,000 is nearly that of pure PHB (+1°C; see Table III below).

Polyvinylacetate (PVAC) was obtained from Wacker-Chemie GmbH (Burghausen, Germany) in granular form, without additives. The viscosity molec-

ular mass M_v of samples was determined by the manufacturer (see Table I).

Molecular mass and polydispersities of the samples were determined by gel permeation chromatography (GPC) using a Waters model 510 pump, Waters model 410 differential refractometer, and Waters model 730 data module with 1000- to 100000-Å Ultrastyragel columns connected in series (Waters Chromatography Division/Millipore, Milford, MA). Chloroform was used as the eluent at a flow rate of 1.5 cm^3/min and polystyrene was used as a standard to calibrate the curve (see Table I).

Preparation of blends

The components, in appropriate weight ratio, were dissolved in chloroform (10% wt/v) under stirring at 70°C. Then the solution was cast onto a glass petri dish, and the solvent was slowly evaporated at room temperature.

Treatment of samples

It is well known that PHB, if it is crystallized at temperatures > 70°C, forms large spherulites with radial and circumferential cracks, as investigated by Barham and coworkers[5,6] [see Fig 1(B)]. Several authors have also stated that large spherulites lead to bad mechanical properties. Therefore, we used the following preparation method.

Samples were prepared by melting the PHB blend between two stainless steel plates at 183°C for 3 min in vacuum and quenching them between two metal plates to room temperature. The resulting sheets (0.4 mm thick) were cut, using a suitable hollow punch, in dumbbell-shape specimens for tensile mechanical testing before measurement. The dumbbell-shape specimens were crystallized isothermally for 3 h at 80°C (a temperature approximating that of maximum crystal growth rate of pure PHB[5]). From morphology observations of these samples (prepared for tensile tests) by optical polarizing microscopy [an example is shown in Fig. 1(A) and (C)], it was decided that the addition of nucleating agents was not necessary in this case.
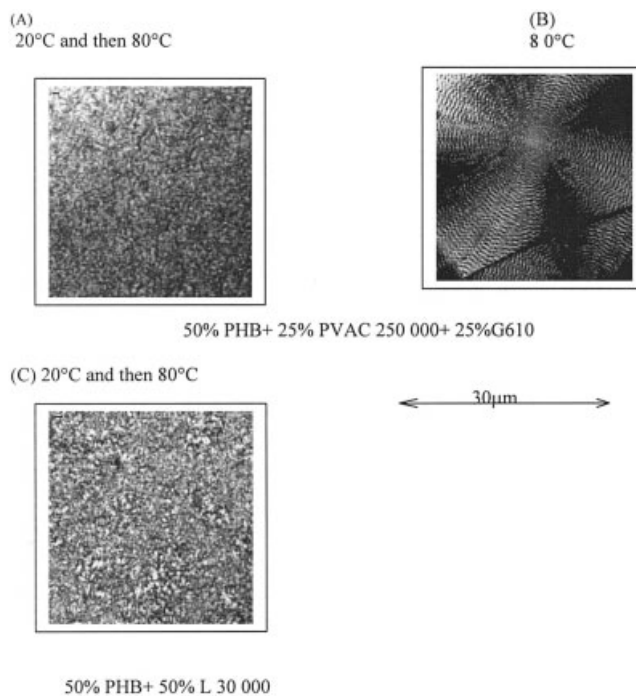

Figure 1 Microphotographs of the morphology of two different blends with 50% PHB (A, C), prepared for tensile testing by the method explained herein, and one (B) cooled directly from 200 to 80°C and crystallized at 80°C for 3 h, for comparison.

Methods

Microscopy

The morphology of the PHB blends was observed with a Zeiss (Oberkochen, Germany) microscope, equipped with crossed polarizers and Linkham hot stage and video attachment.

Tensile testing

Tensile measurements were performed at different temperatures on a Zwick (Ulm, Germany) tensile testing machine model 1445, equipped with a heating chamber, and with an optical measuring system for the sample length. The dumbbell-shape specimens (width = 4 mm, thickness ~ 0.4 mm, L_0 = 13 mm) were usually extended at a rate of 1 mm/min, but some measurements were done at higher strain rates (up to 50 mm/min). To obtain reliable results, the stress–strain experiments were repeated six times for each sample. The stress was calculated as nominal stress (i.e., the quotient of the load force and the initial cross-sectional area). The extension ratio λ is defined as the actual length L divided by the original length L_o, measured between the optical marks in the middle part of specimen.

TABLE I
Properties of Blend Components

Sample code	M_n (g/mol)	M_w (g/mol)	M_v (g/mol)
PHB	300,000	700,000	
PVAC	250,000	730,000	1,100,000
	99,000	200,000	170,000
	23,000	51,000	46,000
L30,000	30,000	55,000	
G974	974	1340	
G610	610	1005	

TABLE II
Properties of Blends with Different Contents of
Plasticizer (Strain Rate: 1 mm/min)

Amount of plasticizer	T_m (°C)	X_c	T_g (°C)	λ_R	σ_R (MPa)
Pure PHB	173	0.65	5	1.01	21
90% PHB + 10% G2670	171	0.62	−13	1.02	15
90% PHB + 10% G610	169	0.60	−25	1.01	13
70% PHB + 30% G2670	167	0.45	−18	1.01	4
70% PHB + 30% G610	165	0.45	−47	1.01	4

DSC measurements

The differential scanning calorimetric measurements were performed on a Q1000-DSC apparatus (TA Instruments, New Castle, DE). Temperature, heat flow rate, and specific heat capacity were calibrated as usual,[29] using indium, sapphire (Al_2O_3), and polystyrene as calibrants. Samples (mass: 4–8 mg) were cut from the drawn region of the test specimens after the tensile test measurements, encapsulated in standard aluminum pans and heated from −80 to 200°C at 10 K/min.

The melting temperature T_m was taken as the maximum temperature of the endothermic peak. The crystallinity X_c was determined from the melting peak area (enthalpy of fusion). The glass-transition temperature T_g was determined from the half-height point of specific heat capacity step.

RESULTS AND DISCUSSION

As mentioned above, there are different factors influencing the tensile properties of PHB blends. In what follows we present the results on the influence of molar mass and glass-transition temperature of the amorphous component, the influence of composition and crystallinity, and the influence of the testing temperature on the tensile properties of the PHB blends.

Influence of glass transition and molar mass of the amorphous phase on mechanical properties

At room temperature, pure PHB exhibits a stress–strain curve typical for a brittle polymer. It is unlike other semicrystalline polymers, where the fracture takes place only after larger extensions, whereas the extension ratio λ_R for samples of pure PHB, prepared as stated above (see sample history), is lower than 1.05 (see Table II). Some authors have attributed this to the fact that PHB has a glass-transition temperature ($T_g = 0 \pm 5°C$) close to the normal testing temperature. Other authors[3,4,8,9,10] correlated the brittleness of PHB to the secondary crystallization: they believe that the secondary crystallization restricts the mobility of the

amorphous phase in interfibrillar or interlamellar regions, resulting in a failure at relatively low strain.

One possible way to overcome the brittleness of PHB would be by blending with low molecular mass oligomers or other plasticizers, to obtain a lower T_g of the blend than that for pure PHB. We used oligomers of atactic R,S-PHB-diol (G610, G2670) as plasticizers, which are amorphous, miscible,[27,30] have a low T_g, and do not evaporate during preparation of the samples (the melting temperature is 183°C). As seen in Table II, the T_g decreases with addition of G610 and G2670, but the extension ratio at rupture λ_R for all of these blends, however, does not exceed 1.02. The major effect of the addition of this plasticizer was to depress the stress at rupture σ_R (see Table II). It should be mentioned that the addition of oligomers not only lowers the T_g but also decreases the average molar mass of the amorphous phase.

To avoid this, we looked for an amorphous polymer with higher molecular mass, but miscible with PHB. Therefore, blends of PHB with atactic R,S-PHB (L30,000), with a higher molar mass ($M_n = 30,000$) than that of the oligomer atactic R,S-PHB-diols, were investigated (Fig. 2). The glass transition of these blends is independent of the composition ($\sim 0°C$), as shown in Table III. The effect of addition of L30,000 on the tensile properties is a reduction of the Young's
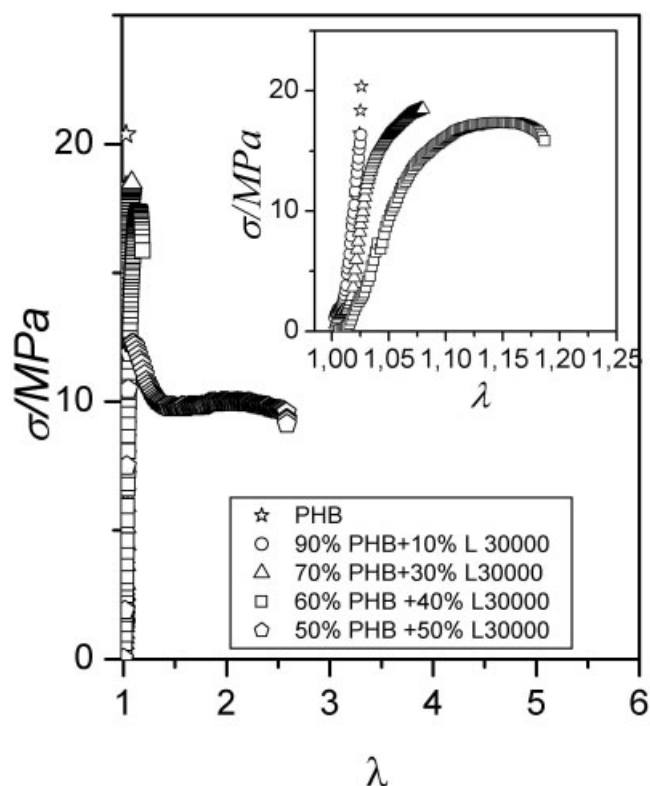

Figure 2 Stress–strain curves of blends of bacterial PHB with atactic R,S-PHB (L30,000) of different compositions as indicated (deformed at 25°C with 1 mm/min).

TABLE III
Properties of Blends with Different Contents of Atactic R,S-PHB (Strain Rate: 1 mm/min)

Amount of L30,000	T_m (°C)	X_c	T_g (°C)	E (MPa)	λ_R	σ_R (MPa)
Pure PHB	173	0.65	5	1800	1.01	21
90% PHB + 10% L	173	0.55	4	1000	1.01	16
70% PHB + 30% L	173	0.44	−1	880	1.08	18
60% PHB + 40% L	171	0.36	2	270	1.18	17
50% PHB + 50% L	171	0.33	3	250	2.5	12
Pure L 30,000	54	0.12	2	—[a]	—[a]	—[a]

[a] Not investigated.

TABLE IV
Properties of Blends with Different Ratios of Plasticizer and Polyvinylacetate (M_n = 250,000; Strain Rate: 1 mm/min)

% PHB : % PVAC : %G610	T_m (°C)	X_c	T_g (°C)	E (MPa)	λ_R	σ_R (MPa)
70 : 30 : 0	170	0.44	34	330	1.09	16
70 : 20 : 10	169	0.48	−5	330	1.21	18
70 : 15 : 15	167	0.45	1	375	1.18	20
70 : 10 : 20	163	0.49	−24	375	1.02	7.5

modulus E and of the stress at rupture σ_R, and an increase of the extension ratio at rupture λ_R. The decrease of E and σ_R can be correlated to a decrease in the crystallinity of PHB (see Table III). For the blend with 50% PHB, the remarkable phenomena of necking, cold drawing, and whitening were observed during the measurement. It should be mentioned that the transition from a rather brittle blend of 70% PHB and 30% L30,000 to a more ductile blend for 50% PHB and 50% L30,000 occurs rather abruptly.

If we compare the strain at rupture λ_R of our blends of PHB with L30,000 with literature values, we find an agreement only for the blend with 50% PHB. For the 75% PHB blend Kumagai and Doi[24] and Abe et al.[23] reported λ_R = 2.5, which is much higher than our value of λ_R = 1.08. The difference may be explained by three reasons: (1) these authors used samples from cast films without further thermal treatment, (2) they used a different strain rate (20 mm/min), and (3) they used samples with a higher molar mass of R,S-atactic PHB with M_n values of 105,000 and 56,000 g/mol, respectively.

Because it was not possible to prepare atactic R,S-PHB with high molecular mass in our laboratory and because it is not commercially available, we used instead PVAC, an amorphous polymer that is miscible with PHB[31] as well and available in grades of various molecular mass.

From the literature it is known that the T_g of the blend increases with increasing concentration of PVAC in the blend,[31] according to the Fox equation. As an example, the T_g of the semicrystalline blend of 70% PHB with 30% PVAC is 34°C (see Table IV), which is too high for good material properties. To obtain a T_g lower than 5°C it was necessary to add some plasticizer; we used the low molecular mass R,S-PHB-diol (G610) for this purpose.

To investigate the effect of the amount of plasticizer (G610) with respect to the PVAC, we prepared a series of blends, as seen in Figure 3. As a result, the blend with equal amounts (1 : 1) of PVAC and G610 had the highest stress at break, and the blend with 10% PVAC and 20% G610 had only very poor tensile properties. If

we compare the glass transition of these blends (see Table IV), we find the lowest glass transition for the sample that has the smallest extension ratio at break λ_R. The results of Figure 3 show the same trend as the addition of oligomers to pure PHB. It must be concluded that the low glass-transition temperature is not the main factor to obtain good tensile properties.

To separate the influence of T_g on the one hand and of the molar mass of the amorphous phase on the other hand, blends of PHB with PVAC of different molecular mass together with G610 (where the ratio of PVAC to G610 was maintained at 1 : 1) were prepared;
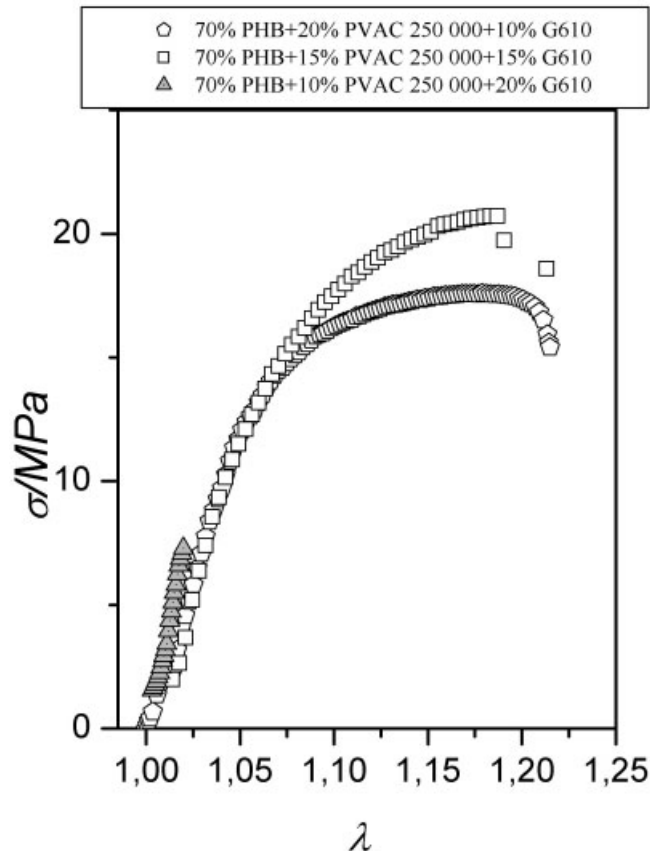

Figure 3 Stress–strain curves of blends of 70% PHB, where the ratio of polyvinylacetate (PVAC) to plasticizer (G610) was varied (deformed at 25°C with 1 mm/min).
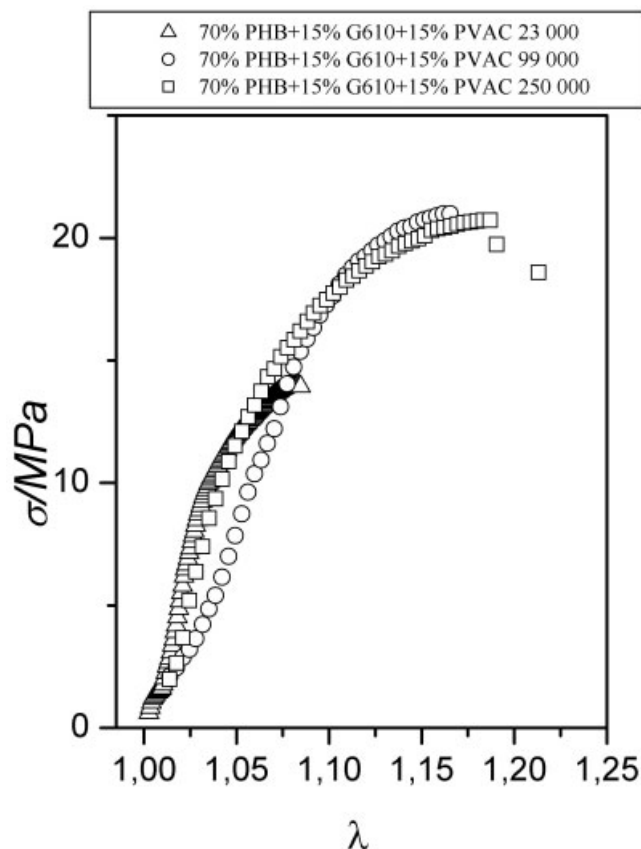
Figure 4 Stress–strain curves of blends of 70% PHB with 15% PVAC of different molecular mass and 15% G610 (deformed at 25°C with 1 mm/min).
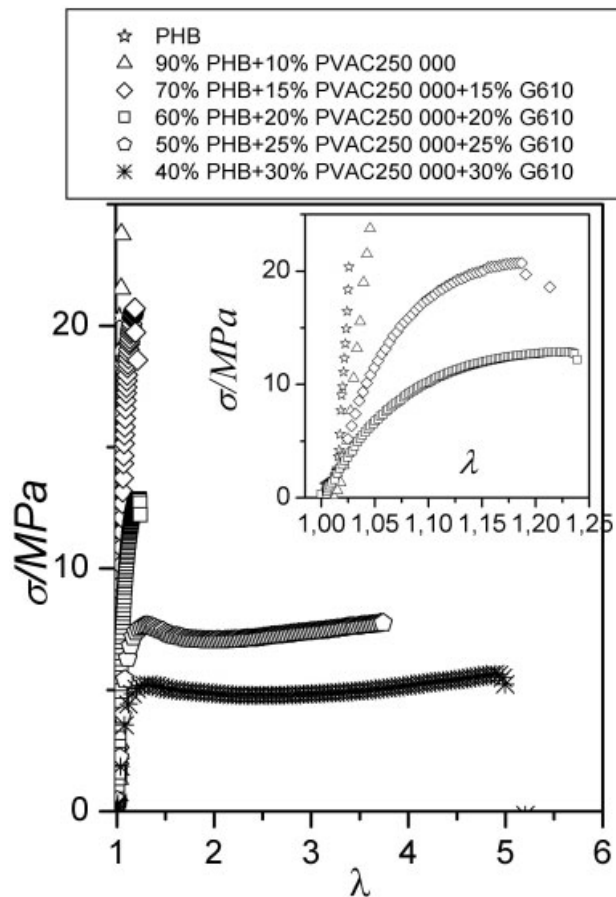

Figure 5 Stress–strain curves of blends of PHB with PVAC and G610 in different compositions (deformed at 25°C with 1 mm/min).

results are shown in Figure 4. The T_g values of these blends are almost the same (see Table V). As can be seen, both the stress and the strain at rupture are strongly dependent on the molecular mass of the amorphous polymer (PVAC).

From all these results obtained for blends of PHB with oligomer *R,S*-PHB-diols, atactic *R,S*-PHB, and PVAC with oligomer *R,S*-PHB-diols, we can conclude that (1) the molecular mass of the amorphous polymers plays an important role in determining the mechanical properties of PHB, and (2) lowering the T_g by addition of low molar mass oligomers, either to pure PHB or to blends of PHB with PVAC, will deteriorate the tensile properties.

TABLE V
Influence of Molecular Mass of PVAC on Blend Properties of 70% PHB + 15% PVAC + 15% G610 (Strain Rate: 1 mm/min)

M_n of PVAC	T_g	E (MPa)	λ_R	σ_R (MPa)
23,000	1°C	400	1.08	14
99,000	1°C	300	1.15	21
250,000	1°C	375	1.18	20

It should be mentioned that El-Hadi et al.[25] measured the extension ratio at break λ_R with a strain rate of 50 mm/min using a blend of 76% PHB with 16% PVAC and 6% tributyrine and 2% 12-hydroxystearic acid. They found a significantly higher λ_R than that of our results (from Fig. 3), although the reason for this large difference is not clear.

Influence of crystallinity and composition on mechanical properties

In this study we investigated a series of blends with equal amounts of PVAC and plasticizer but different PHB fractions (see Fig. 5). In general the overall effect of blending PVAC 250000 and G610 with PHB on the tensile properties is a decrease of Young's modulus and the stress at break, together with an increase of the extension ratio λ_R. Two types of mechanical behavior were found for these blends, depending on the composition. PHB-rich samples (>60 wt % PHB) are characterized by a relatively high tensile modulus and a low extension ratio λ_R. In the case of lower PHB content (<60 wt % PHB) the blends exhibit the typical

TABLE VI
Influence of Composition on Properties of Blends
(Strain Rate: 1 mm/min)

%PHB : %PVAC 250,000 : %G610	T_m (°C)	X_c	T_g (°C)	E (MPa)	λ_R	σ_R (MPa)
100 : 0 : 0	173	0.65	5	1800	1.01	21
90 : 10 : 0	172	0.58	3	970	1.03	25
70 : 15 : 15	167	0.45	1	375	1.18	20
60 : 20 : 20	164	0.39	−6	167	1.24	13
50 : 25 : 25	161	0.36	−11	91	3.75	7.5
40 : 30 : 30	160	0.27	−9	57	5	5.5

necking/cold-drawing effect, together with a lower tensile modulus and higher extension ratio λ_R (see Table VI and Fig. 5). The necking/cold-drawing phenomenon is characterized by semicrystalline polymers being correlated to the beginning of the transformation of the initially spherulitic crystal structure into a fibrillar microstructure.[32–34]

A whitening of the specimen was observed during tensile testing under large deformation. Obviously, crazes are formed in the sample during deformation. Hobbs[9] and Barham[11] observed by electron microscope that PHB undergoes crazing during deformation, regardless of its thermal history.

From Figure 5 it follows that the strain λ at the yield point, for those blends that undergo necking and cold drawing, is approximately equal (in the range $1.1 < \lambda < 1.3$). We also see that the stress at the yield point for the blend with 40% PHB is lower than that for the blend with 50% PHB, which can be attributed to a lower crystallinity (see Table II).

To show more clearly the influence of crystallinity X_c on the extension ratio at rupture for both series of blends (Figs. 2 and 5), λ_R is plotted as a function of X_c in Figure 6. From this figure it follows that higher elongation values ($\lambda_R > 3$) are obtained only if the crystallinity of the blend is below 0.4. It is interesting to note that block copolymers, such as segmental polyester urethane,[17,18] exhibit good mechanical properties only at a PHB content less than 60% and with a crystallinity on the order of 0.4. The same trend was also observed for dry nylon-6 (PA6) by Besselt et al.[36] They found that the mechanical properties depend on the degree of crystallinity and observed that samples with a crystallinity higher than 40% are brittle and samples with 30% crystallinity or lower are ductile.

Influence of testing temperature on mechanical properties

It is well known that tensile behavior greatly depends not only on the experimental conditions, such as strain rate, but also on the testing temperature. The influence of the latter was investigated for several blends (see Table VII), one example of which is shown in Figure 7.
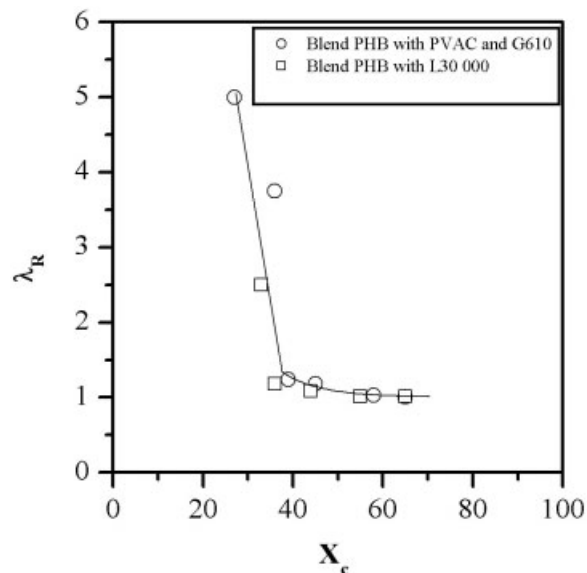

Figure 6 Extension ratio at rupture λ_R as a function of crystallinity X_c of different PHB blends (deformed at 25°C with 1 mm/min).

It is interesting to observe that the extension ratio λ at the yield point remained between 1.1 and 1.2, almost independent of temperature. This is in good agreement with similar results for polyethylene, obtained by Strobl et al.[37,38]

From Figure 7 it follows that the yield strength and tensile strength generally decrease as the temperature increases for the blend of 50% PHB with 25% PVAC and 25% G610. The same was observed for polyethylene[32,37,38] and polypropylene.[39] At higher temperatures (50 and 70°C) we observed that the neck propagates only along a small part of the specimen; at 90°C we did not observe any necking at all. This may confirm why the extension ratio λ_R decreases strongly as

TABLE VII
Influence of Testing Temperature on Properties of Different Blends (Strain Rate: 50 mm/min)

Testing temperature (°C)	λ yield	σ (MPa) yield	λ rupture	σ (MPa) rupture	E (MPa)
		100% PHB			
25			1.01	21	1800
50			1.01	19	1440
70			1.02	15	926
100			1.02	11	446
	50% PHB + 25% G610 + 25% PVAC				
25	1.3	9.6	4.8	11.0	100
50	1.3	7.6	3.1	6.4	69
70	1.25	6.0	1.4	5.5	52
90	—	—	1.15	4.3	40
	40% PHB + 30% G610 + 30% PVAC				
25	1.14	5.2	5	5.5	109
70	1.14	3.4	2.7	2.6	50
90	1.15	2.3	1.3	1.5	31

the temperature increases from 70 to 90°C. A similar trend for tensile tests at elevated temperatures (up to 90°C) was found for the blend with 40% PHB + 30% PVAC + 30% G610 (see Table VII). If we compare the temperature dependency of the tensile properties of our blends to that of other materials, we note that σ_R decreases with increasing temperature. This behavior is well known for all polymeric systems.

However, λ_R shows a different behavior. For slightly crosslinked rubbers above room temperature, λ_R was reported[35] to decrease significantly with increasing temperature. Large strain deformation of semicrystalline polymers is usually discussed in terms of the molecular network, represented by trapped chain entanglements in the amorphous phase and crystallites acting as physical crosslinks.[34,36] For the blends of PHB with high molecular mass PVAC and plasticizer, the decrease of λ_R with temperature means that the orientation of the molecules in the amorphous phase, which is necessary to maintain the stress at high deformations, is lost very quickly at elevated temperature. Additionally, we assume that some of the very thin crystals begin to melt at temperatures above 50°C, so the stability of material is reduced. A small broad peak in the DSC scan (Fig. 8) in the range 50 to 90°C, which was found for samples taken from
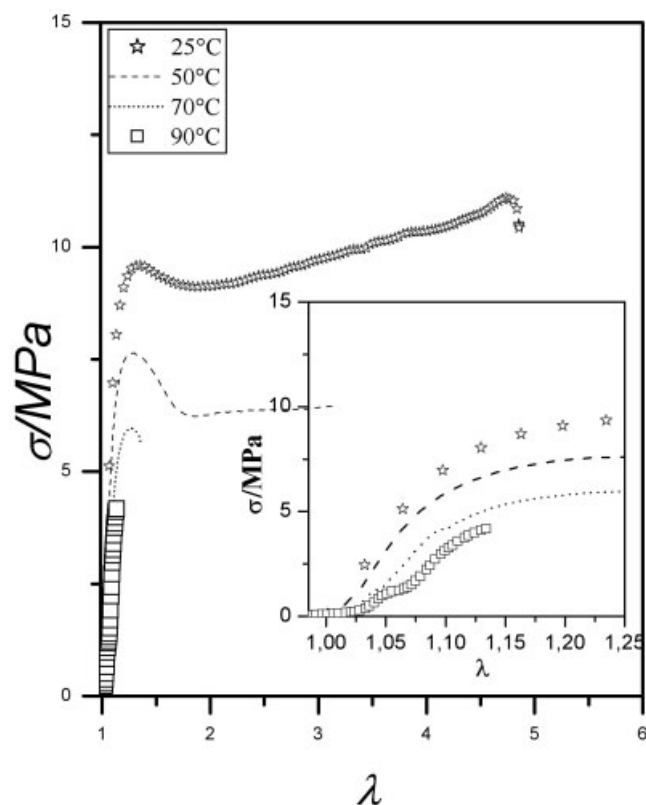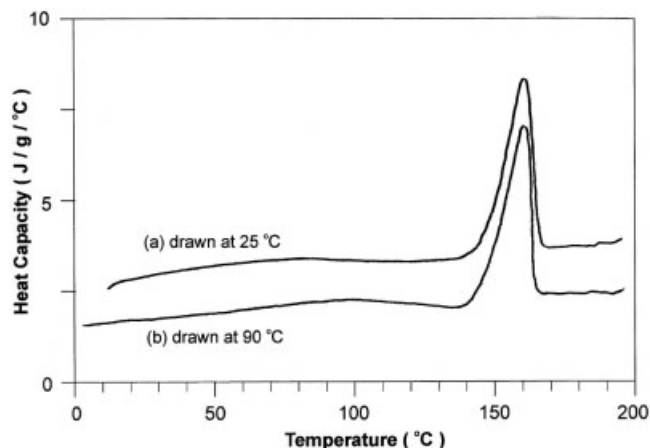

Figure 8 DSC curves of 50% PHB with 25% G610 and 25% PVAC (specimen was taken from the stretched part of the sample drawn at 50 mm/min): (a) drawing temperature 25°C, (b) drawing temperature 90°C.

the drawn region, could be correlated with this phenomenon. On the other hand, polyethylene[32,37,38] and polypropylene[38] exhibit large λ_R up to temperatures close to the melting point. This may be attributable to the higher number of tie molecules (which are running from one crystal lamellae to the next, connecting neighboring lamellae) in PE and PP compared to that of our blends. Because of these reasons the temperature range for technical applications of these blends (see Fig. 7 and Table VII) is limited.

Tensile tests (in the temperature range from 25 to 100°C) have also been done with pure semicrystalline PHB (see Table VII). It was found that the extension ratio at break is independent of the testing temperature ($\lambda_R = 1.02$), whereas σ_R decreases with increasing temperature. This result is in good agreement with the results reported for molded PHB, which was stored 400 days at room temperature,[3] and also with results reported by Bauer and Owen.[40] On the other hand, Barham et al.[7] found a significant increase of λ_R at higher temperature (100°C). The reason for this experimental discrepancy may be the different sample preparations, given that Barham et al.[7] used samples from a solution-cast film without further thermal treatment.

Influence of strain rate on mechanical properties

It was interesting to investigate the effect of strain rate on the stress–strain curves for the blend with 50% PHB + 25% PVAC + 25% G610 (see Fig. 9). As a result it can be stated that with increasing strain rate, the yield stress increases. The larger the strain rate, the lower the time available for the amorphous chains to rearrange according to the applied deformation; as a result the yield stress at 50 mm/min is higher than at 1 mm/min. Furthermore, with increasing strain rate the
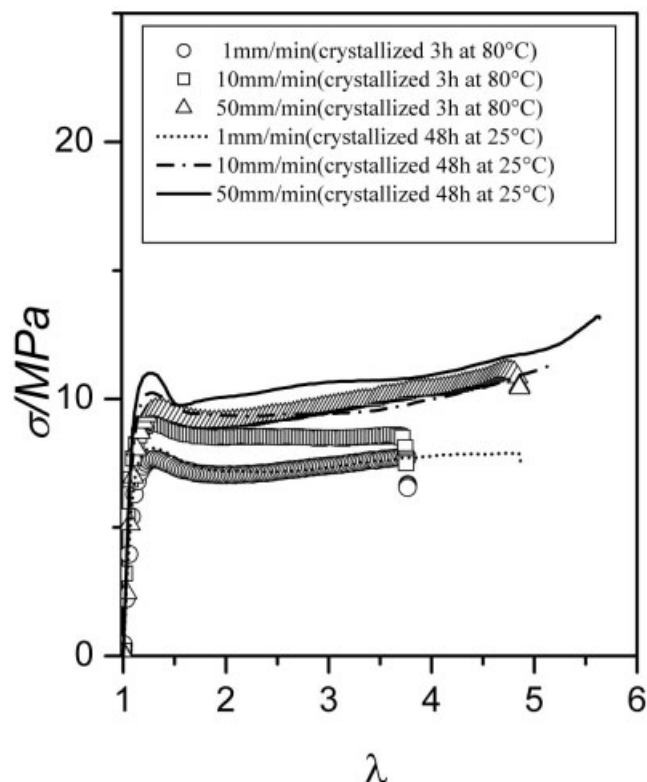

Figure 7 Stress–strain curves of blends of 50% PHB with 25% PVAC and 25% G610 at different temperatures (draw rate: 50 mm/min).

Figure 9 Stress–strain curves of blends of 50% PHB with 25% PVAC and 25% G610 measured with different strain rates at 25°C.

sudden drop in stress shortly after the yield point (which is caused by the reduction of the cross section of the specimen after necking) decreases. This was also found for polypropylene.[39]

A strain hardening effect (irreversible increase of σ at high elongations; see Fig. 9) is visible only in the curve with 50 mm/min deformation rate in the region $\lambda > 4$. It is known that strain hardening in semicrystalline polymers like polypropylene[39] is more pronounced at higher strain rates, which is in agreement with our results.

To sum up, when comparing Figures 7 and 9, it follows that the deformation behavior changes in the same way on increasing temperature as on decreasing strain rate. Increasing the deformation temperature from 25 to 50°C has nearly the same effect on both the tensile strength and the extension ratio λ_R as that of decreasing the strain rate from 50 to 1 mm/min.

Influence of ageing and annealing on mechanical properties

To test the long-term stability of our materials, stress–strain experiments of the blend 50% PHB + 25% PVAC + 25% G610, after different storage conditions, were performed at a strain rate of 50 mm/min. The following conditions were used: storage at room tem-

perature for 1 month (see Table VIII), annealing at 105°C for 2 h, or crystallization for 48 h at room temperature instead of 80°C (results in Fig. 9). No significant change of the extension ratio λ_R at rupture was found in these cases. This may be attributable to the depression of the secondary crystallization for these blends relative to that of pure PHB, an explanation in agreement with the interpretation in Hay and Sharma.[41]

CONCLUSION

1. In contrast to some authors who reported that the high T_g of PHB is the main factor responsible for deterioration of its mechanical properties,[3,5,8] our experimental finding is that lowering T_g, by addition of low molecular mass additives, deteriorates the tensile properties of PHB (σ_R decreases, λ_R decreases below 1.02).
2. At elevated testing temperatures, the blends of 40 and 50% PHB, which exhibit necking and cold drawing at room temperature, show a significant decrease of the extension ratio at break λ_R, which seriously limits the technical application temperature range.
3. To obtain good mechanical properties of blends of PHB with miscible amorphous components (extension ratio $\lambda_R > 3$), we suggest that the average molar mass of the amorphous component should be $M_n > 30{,}000$ g/mol, and that the content of PHB should be less than 60%, leading to a crystallinity less than 0.4%.

TABLE VIII
Influence of Strain Rate and Storage Time on Properties of the Blend 50% PHB + 25% PVAC + 25% G610

Strain rate (mm/min)	λ yield	σ (MPa) yield	λ rupture	σ (MPa) rupture
Crystallized 2 h at 80°C				
1		7.5	3.75	7.5
10		9	3.8	8.5
50		9.6	4.8	11
Crystallized 48 h at 25°C				
1		8	4.8	7.5
10		10.5	5.1	11
50		11	5.6	13
Crystallized 2 h at 80°C and stored 1 month at 25°C				
50		9.5	5.4	9

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