DOI: 10.1002/masy.200950521

Biodegradable Poly(3-hydroxybutyrate) Nanocomposite

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Summary: This work seeks bringing a technological and social contribution by searching blends and composites of poly(3-hydroxybutyrate) (PHB) and polyethylene widely used in packaging films, and colloidal silica. The mixtures were prepared by extrusion using a single-screw extruder and were analyzed regarding their thermal and mechanical properties and morphology. The results have shown PHB toughness in the studied compositions, which elongation at break was in the range 5–80% compared to 2% for neat PHB. The small amount (0.2 to 0.4%) of added silica seemed to increase in 20% the tensile strength. The thermal degradation by thermogravimetry from room temperature to 800 °C revealed a mixed behavior for the composites between PHB and polyethylene.

Keywords: biodegradable; blends; PHB; polyethylene

Introduction

Among the biodegradable polymers, poly (3-hydroxybutyrate) (PHB) is well- known. PHB is commercially available and has been produced by PHB Industrial S.A. (Brazil) since 2000 from bacterial fermentation,[1] by a process that is integrated into the sugarcane mills, associated to the production of the commodities sugar and alcohol. Under pilot scale production (50 ton/year), the price of PHB (Brazil) amounts to US$3.00–5.00/kg, however with an estimated production of 30,000 ton/year in a new industrial project[2] figures may change. The major drawbacks of PHB are its hardness and brittleness (small values of elongation at break) and high cost. Several factors can contribute to the improvement of the mechanical properties of PHB, as addition of nucleating and plasticizing agents, as well as the modification of PHB structure leading to new bacterial copolymers, poly(hydroxybutyrate-co-hydroxyvalerate) (PHBHV). There are some studies focusing blends and composites of PHBHV, which is much more flexible than PHB,[3–11] and the reported results have demonstrated mechanical reinforcement, however PHBHV is very expensive, the copolymer containing 10% of HV is calculated to cost US$3.95/kg in a 100,000 ton/year plant[12] compared to 2.65/kg for PHB at same production scale.[13]

Actually, the most economical method is the blending with other polymers. The properties of the polymer blend in turn will be dependent on the degree of miscibility of the polymers. Blending of PHB with other polymers have been reported by many authors,[14–19] working with poly(ethylene oxide),[20,21] poly(vinyl fluoride), poly(vinyl acetate), poly(vinyl alcohol)[15,16] and biodegradable bacterial and synthesized aliphatic polyesters,[15–19] among others, included in a recent review by Ha and Cho.[22] Blends of PHB and poly(ethylene oxide)(PEO) ($M_w = 2 \times 10^4$ g/mol) were first studied by

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Avella and Martuscelli[21] and, later, received further attention from Martuscelli's group,[23,24] Kumagai and Doi,[25] Inoue's group (PEO, $M_v = 3 \times 10^5$ g/mol),[26,27] You et al. (PEO, $M_v = 5 \times 10^3$ g/mol)[28] and Parra et al. (PEO, $M_n = 3 \times 10^2$ g/mol).[29] PHB and poly(ethylene oxide) blends were prepared in all composition range and have been found to be miscible in the melt state and in the amorphous phase, while the melting temperatures of both crystalline phases have been observed to remain essentially invariable.

According to Ray and Bousmina,[10] the biodegradable composites portray optimistic future perspectives, however the present low volume production and their high cost restrict their usage in large scale. Toth et al.[30] reported on the application of an atomistic modeling in the investigation of the structure, morphology and energetic differences of polymer nanocomposites based on non-steroidal anti-inflammatory drugs (NSAIDS), hydrotalcites, PHB and PVA. Yew et al.[31] have prepared composites of PHB containing up to 57% of TiO_2 nanoparticles (50 m^2/g) by dissolution in $CHCl_3$. The composite films presented antibacterial activity. To our knowledge, Maiti et al.[32] have prepared the first PHB nanocomposite with organophilic clay through melting intercalation in a twin-screw extruder, however the nanocomposites of montmorilonite presented severe degradation during processing, although no degradation was observed for those with fluoromica.

This work investigates blends and composites of PHB and polyethylene, using poly(ethylene glycol) ($M_n = 300$ g/mol) or poly(propylene glycol) ($M_n = 4000$ g/mol) as a plasticizer, and colloidal silica, aiming for novel disposable generally purpose packaging films and fibers.

Experimental Part

Materials

Poly(3-hydroxybutyrate) (PHB) was supplied by PHB do Brasil S.A., Usina da Pedra, Brazil, and used without further purification. Polyethylene (PE) (Trithene®) was kindly provided by Petroquímica Triunfo, Brazil. Poly(propylene glycol) ($M_n = 4000$ g/mol) (Arch Chemicals, USA) (plasticizer 1) or poly(ethylene glycol) ($M_n = 300$ g/mol) (Oxiteno, Brazil) (plasticizer 2) was used as a plasticizing agent for PHB and colloidal silica (CAB-O-SIL LM-150) (Degussa, USA) was used for mechanical strengthening purpose.

Blends and Composites Preparation

The blends and composites were prepared by melt extrusion using a single screw extruder (diameter = 2.54 mm, L/D = 20 and 45 RPM) (Gentil, Brazil), three heating zones set at 110, 150 and 170 °C, and feeding of 25 g/min.

Blends and Composites Characterization

Tensile tests were performed on injected specimens (Haake Minijet II, Thermo Fischer Scientific), using a Kratos Universal Testing Machine at 10 mm/min, according to ASTM D-638. All tests were performed at room temperature and 50% humidity A Shimadzu A50 was employed for DSC measurements under nitrogen atmosphere. Each sample was first heated from room temperature to 150 °C or 200 °C at a rate of 10 °C/min followed by quenching to −65 °C. A second heating cycle was applied at a rate of 10 °C/min and the T_g and T_m values were taken as the midpoint of the specific heat jump and the peak maximum, respectively, observed in the second scan. TGA runs were performed using a TGA51 equipment (Shimadzu), under argon flux. Samples of about 10–15 mg were heated up to 800 °C at a rate of 10 °C/min. A Philips XL-30 Scanning Electron Microscope was used for morphology characterization of the cryogenically fractured surfaces. The samples were submitted to gold sputtering to make them conductive prior to the analyses. Magnifications of 300× to 20,000× were applied to each sample to estimate the domain sizes.

Table 1.
Composition of blends and composites.

Blend/composite	PHB %	PE %	Plasticizer 1 %	Plasticizer 2 %	SiO_2 %
1	16.13	80.65	3.22	–	–
2	22.06	73.53	4.41	–	–
3	16.08	80.38	3.22	–	0.32
4	21.96	73.21	4.39	–	0.44
5	25.11	71.73	2.87	–	0.29
6	27.70	69.25	2.77	–	0.28
7	4.74	94.79	–	0.47	–
8	9.01	90.09	–	0.90	–
9	16.39	81.97	–	1.64	–
10	22.56	75.19	–	2.25	–
11	28.78	69.44	–	2.78	–
12	16.37	81.83	–	1.64	0.16
13	8.81	89.13	–	1.78	0.18
14	16.08	80.39	–	3.22	0.32
15	21.96	73.06	–	4.39	0.44

Results and Discussion

The blends and composites (Table 1) were prepared by extrusion using a single-screw extruder and the mixtures, thus prepared were analyzed regarding their thermal and mechanical properties and morphology.

The tensile properties of the blends and composites (Table 2) are presented in comparison to that of neat PHB. A noteworthy increase of the elongation at break indicates a toughening effect by plasticizing PHB and blending with PE.

The results of the mechanical tests (Table 2) were obtained from at least five and maximum of 13 test specimens. Increasing the amount of PHB in the composites lowered the elongation at break, although no significant increase on the tensile strength was observed. Mixing with polyethylene reduces the Young's modulus of PHB to about one third to one tenth of its original value. This behavior was expected, since PE has a low modulus, about 85 MPa, consequently the mixtures displayed an intermediate value between that of PHB and PE.

The stress at break provided by the blends and composites (2.70–6.61 MPa) is lower or close to that of PE. As the major component, PE, represents the matrix, poor adhesion among the components might

Table 2.
Mechanical properties of blends and composites compared to the polymers.

Sample	E (MPa)	σ_Y (MPa)	σ_R (MPa)	%ε (%)
PHB	1045 ± 66	8.68 ± 0.93	8.84 ± 0.76	1.84 ± 0.40
PE	84 ± 7	6.17 ± 0.42	6.12 ± 0.53	100.11 ± 13.37
1	111 ± 11	7.50 ± 0.40	6.52 ± 0.85	82.79 ± 19.73
2	132 ± 6	5.87 ± 0.26	3.79 ± 0.48	37.28 ± 13.67
3	152 ± 11	8.67 ± 0.17	6.61 ± 0.61	78.29 ± 10.56
4	122 ± 10	6.70 ± 0.49	5.60 ± 0.60	44.79 ± 10.49
5	174 ± 8	7.10 ± 0.25	5.45 ± 0.46	34.93 ± 3.47
6	128 ± 17	8.19 ± 0.73	6.14 ± 1.24	30.09 ± 3.73
7	140 ± 21	3.56 ± 0.30	5.49 ± 0.29	19.69 ± 4.23
8	146 ± 17	2.06 ± 0.33	3.81 ± 0.47	6.45 ± 1.46
9	260 ± 54	4.01 ± 0.30	5.70 ± 0.72	8.00 ± 1.50
10	232 ± 40	2.48 ± 0.28	2.70 ± 0.28	2.90 ± 0.57
11	332 ± 50	2.91 ± 0.29	3.00 ± 0.33	2.16 ± 0.28
12	187 ± 16	3.75 ± 0.23	4.63 ± 0.20	11.52 ± 2.40
13	139 ± 18	3.46 ± 0.38	4.41 ± 0.46	10.8 ± 1.53
14	257 ± 49	4.34 ± 0.41	4.70 ± 0.54	10.0 ± 2.06
15	209 ± 37	3.20 ± 0.50	3.60 ± 0.81	5.60 ± 1.73

causes the premature fail. The ultimate strain of the blends and composites, however, were much higher than that of PHB (1.84%), from 2.16% to 82.79%, proving that the mixing process toughened PHB. This last result is very important, since the PHB major drawbacks are its hardness and brittleness, as small values of elongation to break (<3%) are reported by several studies.

The results have shown PHB toughness in the studied compositions, however the increment of the ultimate strain was more effective in the compositions 1–6, compared to 7–15. The addition of silica, even in that small concentration (0.2 to 0.4%), had a strong effect on the mechanical properties of the nanocomposites 3–6. Composites 3 and 4 have the same polymer matrix found in blends 1 and 2, respectively. The comparison of the results of the tensile tests shows that the addition of the silica, even in minute amount is very favourable, and a 20% increase in the yield and tensile strengths occured after 0.3–0.4% of silica, while no significant change in ductility was observed.

According to the miscibility of the components in a binary polymer blend, it can be classified into three types, namely, completely miscible, partially miscible and completely immiscible polymer blends. PHB and PE are known to be completely immiscibility polymers, and the T_g's of the polymers in the blend are close to those of neat components, however, in the results here shown, nonetheless some mechanical properties of PHB have been improved by mixing PE.

The DSCs curves (Figure 1) show the melting of the crystalline phases, T_m's of PHB and polyethylene, as well as the cold crystallization of PHB (T_c).

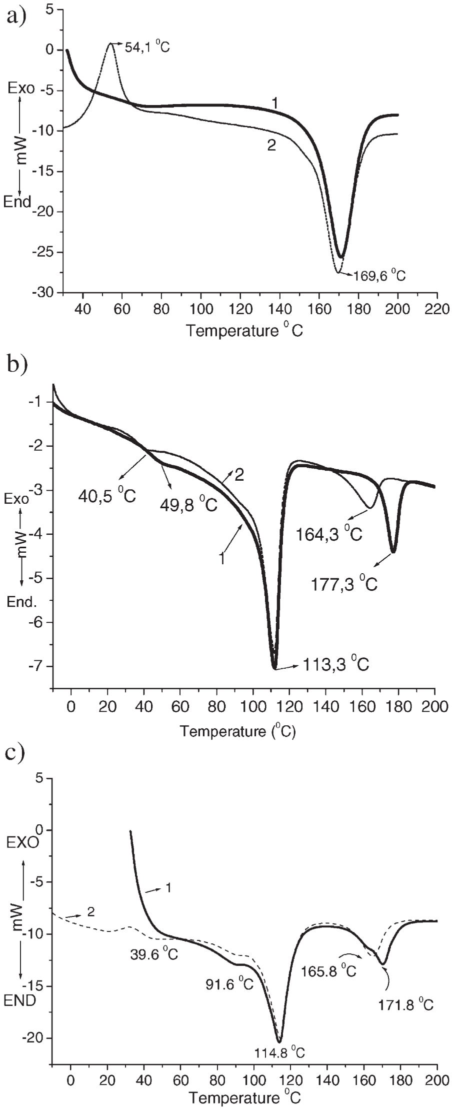


Figure 1.
DSC curves indicating first (1) and second (2) heating cycle are shown for (a) PHB; (b) blend 9; and (c) composite 15.

PHB in the mixture presented melting peak in the range 170–176 °C, higher than neat PHB (169 °C), this result suggested that PHB crystalline lamellas are thicker or crystallites are more perfect in the blends and composites. However, after quenching, the second heating cycle showed a reduced T_m for PHB (164 °C) for the samples 7–15, indicating the preponderance of the chain orientation, due to the extrusion before the first heating cycle, as well as the sample thermal history on the crystallization and melting of PHB. Furthermore, the DSC curves (Figure 1a, 1c and 2) clearly showed a cold crystallization of PHB in the second heating cycle after quenching, which indicates restriction

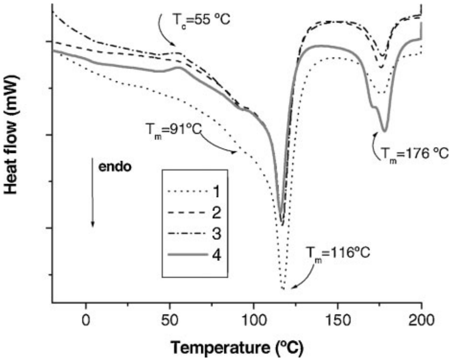


Figure 2.
DSC curves showing the second heating cycle.

for molecular folding during the quenching to room temperature from the melt.

The absence of the cold crystallization peak of PHB in the blends (1,2 and 7–11), suggests that the flexibility of the polymer blend matrix containing polyethylene is very favorable for the PHB crystallization upon quenching. However, around 40–50 °C, cold crystallization was observed in the nanocomposites (3–6 and 12–15), the presence of the microconstituent colloidal silica seems to affect PHB crystallization rate after quenching from the melt, which is credited to the interactions at the polymer-filler interface. According to Capitán et al.[33] the polar groups of PHB interact with those of the glass substrate leading the polymer chains to suffer a strong constraint that prevents PHB crystallization.

The TGA curves of the blends and composites are shown in Figure 3 in comparison with those of polyethylene and PHB. Both types of mixture presented lower onset degradation temperature compared to pure PHB. The blends and composites presented two main degradation steps in the ranges 275–300 °C and 400–500 °C, ascribed to PHB and polyethylene thermal degradation, respectively. The mass lost in the first degradation step is proportional to the PHB content in the mixture. The blends and composites presented intermediate thermal stability compared to PHB and polyethylene, and the mixed behavior indicates good dispersion of the components, although no miscibility is believed to occur.

The samples were examined by scanning electron microscopy (SEM) in order to check the morphology. The mixtures 1–6 did not present coarse particles expected for the PHB dispersed phase, although a small number of aggregates and large particles are believed to have been detached from the matrix (Figure 4a and 4b), nonetheless they did not seem to be representative. In contrast, in the mixtures 7–15 micron-sized particles of PHB are easily observable, forming uniform spherical dispersion within the matrix.

At higher magnification (20,000×) it was possible to distinguish buried particles of colloidal silica (Figure 4c) in the composites, which are in the nanometer range.

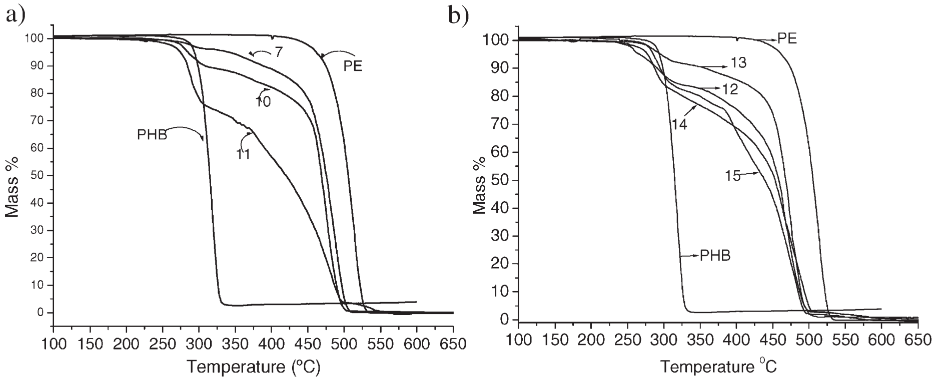
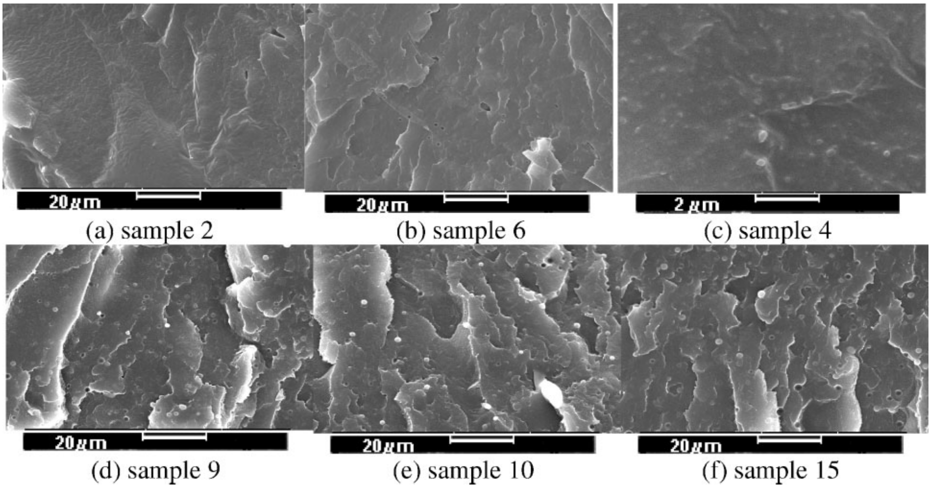


Figure 3.
TGA curves of PHB and PE, (a) blends and (b) composites.



(a) sample 2 (b) sample 6 (c) sample 4
(d) sample 9 (e) sample 10 (f) sample 15

Figure 4.
SEM of the mixtures taken at 3,000× and 20,000× of magnification.

The composites 3–6 presented more uniform polymer matrix compared to those of 12–15, which may explain the higher elongation at break observed for the preceding samples. For those composites, although a comparative reduction of the modulus of elasticity was observed, the yield and tensile strengths were enhanced.

Acknowledgements: The authors thank FAPESP, CNPq and Petrobras for financial support. We also thank PHB Industrial S.A., Petroquímica Triunfo and Oxiteno for donation of PHB, polyethylene Trithene and poly(ethylene glycol) PEG300, respectively.

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