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Thermal and dynamic mechanical properties of binary blends of bacterial copolyester poly(hydroxybutyrate-co-hydroxyvalerate) (PHBHV) with poly(2-hydroxyethylmethacrylate) (PHEMA)

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Poly(hydroxyalkanoates) (PHAs) are natural polyesters produced by microorganisms [1–3]. In order to improve mechanical properties and reduce its cost, blending of natural PHBHV with synthetic polymers has been performed [1]. PHBHV is a semi-crystalline, biodegradable, thermoplastic polymer synthesized by many different kinds of bacteria [4]. Miscible and immiscible blends of PHBHV with synthetic polymers have been obtained [2]. Blends of semi-crystalline and amorphous polymers can result in miscibility of both components. PHBHV has been blended with amorphous polymers to allow a decrease in its [5], translating it into a better processability. Surface and internal mechanical properties of polymeric solids might be closely related to the thermal molecular motion and the aggregation state on the surface, which are thought to be directly associated with the inherent properties of polymers such as the glass transition temperature, T_g [6]. In this study, the thermal and dynamic mechanical properties of bacterial poly(3-hydroxybutiric-3-hydroxyvaleric acid) (PHBHV, 21 mol% of 3 HV units), poly(2-hydroxyethylmethacrylate) (PHEMA) and their blends prepared by slowly casting are presented.

PHB-21%HV was obtained by methods previously reported [4]. The blends were prepared by slowly casting films using chloroform as a solvent. The compositions were explored in a range of 20–50% PHEMA on PHBHV.

The thermal behavior of the polymers was determined with a 951 TA-DSC module linked to a thermal analyzer 2100 microprocessor, at a heating rate of 10 °C min^{-1} under nitrogen or air flow (50 × 10^{-6} m^3 min^{-1}). The first run was carried out from –50 to 200 °C to determine melting temperature (T_m). Glass transition (T_g) values were obtained through a second run in the same temperature range (middle point).

Dynamic mechanical properties were evaluated on the films. The tensioned films tests were performed at 1 Hz. The range of temperatures tested was from –50 to 200 °C (ramp of 10 °C min^{-1}). Film crystallinity was measured with a Rigaku diffractometer (Cu K_α). The angular range measured (2θ) was from 5.0° to 60°.

Results of DSC thermograms obtained are shown in Table I. The thermogram of pure PHBHV showed the typical behavior of a thermoplastic reported in a previous paper [4]. T_g values of PHB-21%HV and PHEMA were −4 and 42 °C respectively. The T_g values of PHBHV in the PHBHV-PHEMA blends were almost independent of the blend composition. The T_m of PHBHV was determined at 85 °C. One glass transition was observed in the thermograms of the blends (around of −4 °C), a value that corresponds to that registered for PHBHV. We could observe an isothermal of crystallization for pure PHBHV at 40 °C. The results of thermal characterization of pure PHB-21%HV were similar to those reported for a similar monomer composition [7].

The DSC thermogram of the blends exhibited an exothermal peak, similar to the isothermal crystallization of pure PHBHV at 41 °C. In all studied blends, the isothermal of crystallization was observed. The melt transition was observed in the range of 75 to 95 °C for all the blends.

In Table I the loss factor of bacterial copolymer PHBHV, PHEMA, and their blends are reported. The technique of DMA is very sensitive to the molecular motions; in this sense, in the thermograms, we could observe that PHBHV (tan δ) presents the transitions α and β previously described by other authors [1]. The zone in the vicinity of α transition is associated whit T_g according to Lotti *et al.* [1]. The storage modulus (G') showed a similar behavior to that reported for

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TABLE I Results of DSC experiments and degree of crystallinity

PHBHV/PHEMA (% w/% w)	T_g (°C)	T_c (°C)	T_m (°C)	Crystallinity[a] (%)	G' (MPa)
100/0	−4.0	41	85	53	1400
80/20	−4.0	40	83	52	1150
70/30	−2.0	42	81	53	700
50/50	−5.0	43	84	51	800
0/100	42	–	–	0	1300

[a] The crystallinity was measured by X-rays.

PHB—20%HV [8]. A relaxation associated with the crystallization at 45 °C, similar to that determined by DSC could be observed. For pure PHEMA the maximum value of storage modulus was 1300 MPa at room temperature. We observed that the results of DSC and DMA tests are independent from the composition of the blends (Table I) and infer immiscibility of both components.

Tensile strain analysis showed that with the increment of the PHEMA content from 0 to 50%, the module of elasticity of the PHBHV/PHEMA blends decreased from 1400 to 800 MPa. The maximum values of tan δ as function of PHBHV content are shown in the Fig. 1. Maximum and minimum values of tan δ were 1.04 and 0.42, which correspond to a 50:50 blend and pure PHBHV, respectively.

The crystallinity of the blends, measured by X-rays, showed no changes with regard to pure PHBHV (Table I). X-ray patterns of samples were almost the same as observed for pure PHBHV (Fig. 2). The percentages of crystallization of pure PHBHV and its blends with PHEMA were in the range of 50–55%, that are in agreement with those obtained by others [9, 10]. These results are shown in Table I. Thermal characteristics of PHBHV were also previously reported for PHAs [7]. The width of the fusion signal was greater than that observed for PHB, phenomenon associated whit the isodimorphism in copolymers [11, 12]. The melting transition of PHBHV (21% HV) was minor in comparison with the PHB—18%HV (92 °C), possibly due to the effect of heating rate. The DSC results showed an independence of the T_m and T_g values of the blends from the PHEMA content. The crystallization peaks overlapped the second glass transition that corresponds to PHEMA. Koyama and Doi [13] showed similar results when blending PHB with poly(ε-caprolactone-co-18% lactide).

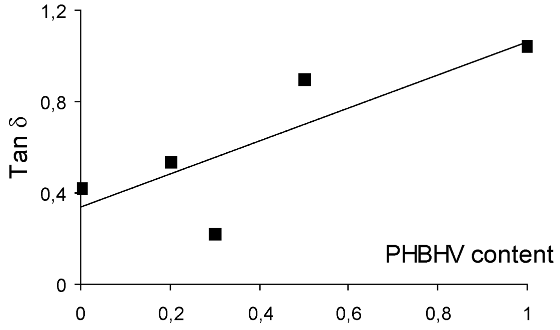

Figure 1 Dependence between PHEMA content and tan δ.

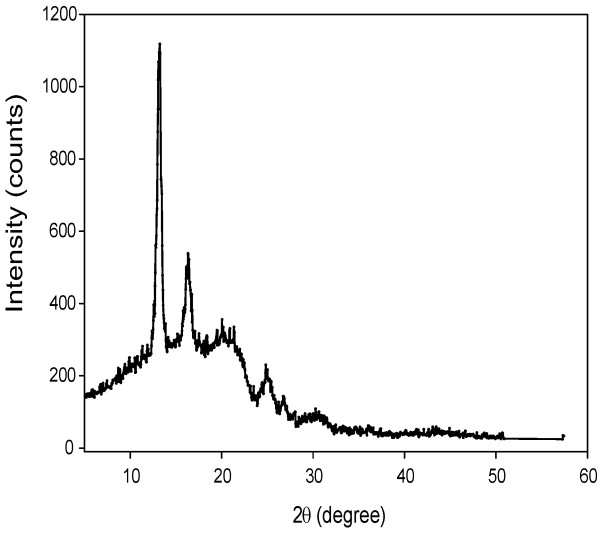

Figure 2 X-rays pattern of PHBHV sample.

The DMA results showed that when PHEMA content increased tan δ decreased suggesting that the blended components were only physically mixed, without interaction between the polymers. The DMA results indicated that PHEMA remarkably do not affect the crystallization behavior of PHBHV and nor make the PHBHV/PHEMA blends more flexible and elastic. These results are in concord to the data reported for PHB/PHBHHx blends by Kai *et al.* [14]. In a previous paper, we reported that the surface of the blends obtained is irregular and heterogeneous with a porous texture similar to that of pure PHBHV [15]. This porous texture of PHAs has been reported previously [16] and together with the present results, we inferred that the surface consisted of a PHBHV-rich phase. Moreover, in our previous paper we did not observe changes in the crystallinity of the blends in comparison with the pure PHBHV. The immiscible character of these blends can be attributed to the non-existence of an intimate contact between the components, and the accumulation of the microbial polymer at the surface. The presence of two phases in the blends reported before [15] were also found by Lee [6], since the surface of a multiphase polymer blend is enriched by a component that has lower surface free energy. These DSC thermograms confirm that the blends are immiscible. Our observations are in close agreement with other experiments where immiscibility was observed using a biological PHBHV and polyalcohols [17], although it is not possible to make precise comparisons with other works due to the differences that exist in the experimental conditions. The X-rays results also confirm the immiscibility of the blends.

The blends of PHB-21HV with PHEMA showed poor compatibility. The immiscibility of both polymers has been confirmed through investigations on thermal, X-rays and mechanical behavior of their tested blends.

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