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HV CONTENT EFFECT ON THERMAL, MORPHOLOGICAL AND MECHANICAL PROPERTIES OF PHBHV PRODUCED BY FED-BATCH CULTURE OF *Ralstonia eutropha*

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Abstract

The ratio of butyric acid (Sb) and valeric acid (Sv) in the fresh medium has an effect on the HV content of PHBHV copolymer produced by *Ralstonia eutropha*. 40% of HV units can obtain with a medium with mole ratio of fatty acid concentrations (Sv/ (Sb+Sv)) around 0.75. Storage modulus (G') increasing depending on the HV units increase. The results showed that the maximum value of both modulus (G', G'') are higher than the homopolymer PHB. The glass transition of PHBHV samples were around of -7° C to 1° C. In this work we present the results of DSC, X-rays and DMA studies for PHBHV samples with different compositions of the comonomers.

INTRODUCTION

Poly(hydroxybutyrate -co- hydroxyvalerate) (PHBHV) is a biodegradable polyester of industrial interest. It has been reported that composition and properties of PHBHV depends on HV content ¹, the carbon source supplied ² and the mole fraction of substrates in the feeding medium ^{3,4}.

The aim of this work was to correlate the thermal, morphological and mechanical properties with the HV units in PHBHV.

MATERIALS

Fed-batch cultures of *R. eutropha* ATCC 17699 were performed in order to produce PHBHV, at different molar ratio of fatty acids, Sv/Sv+Sb, in the range 0-0.75. The cultures were carried out in a 5L fermentor (Bioflo III, New Brunswick Co). PHBHV and PHB were extracted from lyophilized cells with hot chloroform, and purified by reprecipitation with hexane.

The HB and HV units in polyesters were determine by ¹H NMR analysis with CDCl₃ (300 MHz, Mercury 300, Varian). The glass transition and melting temperature were determinate from DSC (Dupont 910) after the samples were cooled down to -50° C. The samples were heated up to 200° C at 10

°C/min (run I), for estimate melting temperature and ΔHf, and in the second run it was estimated the glass transition temperature (Tg) (onset). The x-ray analysis was performed using a horizontal goniometer (Philips 1138) coupled with a generator of high stability (Philips 1160) and associated electronics. Dynamic mechanical tests were carried out in the glass-rubber transition temperature range with a TA (DMA 2980 TA instruments). The specimen was a thin film with dimensions around of 25 mm x 8 mm x 0.1 mm. Measurements were performed at 1 Hz between -50 and 200° C. The heating rate was 10° C min⁻¹.

RESULTS AND DISCUSSION

The results show that %HV unit incorporated in the copolymer is not related proportionally with valeric acid feeding, which suggest a limit on utilization of this fatty acid. Instead, the relation between %HV unit in PHBHV and molar ratio of fatty acids feeding is linear. Table I shows the mole fraction HB and HV units in PHBHV obtained and its relation with mole ratio of fatty acid concentrations (Sv/(Sb+Sv)) present in feeding medium.

In figure 1 is shown the dependence of Tg with %HV unit. Tg values decrease as %HV

units in the copolymer increase, but this decrement is low (0.6°C for 0% to -7.4°C for 38%). In Table II is shown the thermal properties for the samples. The crystal grown, nucleation and morphology of PHB are in many way typical for polymers, however the PHBHV copolymers have high crystallinities (% χ , see Table II) at all compositions. Since the copolymers are random, it implies that the two comonomers must cocrystallize⁶. In copolymers with less than 30% HV crystallize with the PHB structure while the sample with more than 49% HV have the PHV structure. Both structure are present at intermediate composition (35 y 38% HV); therefore, we have two fusion temperatures for these samples. The first fusion temperature (Tf1) decrease as %HV increase while the second fusion temperature (Tf2) is almost constant.

TABLE I. RELATION BETWEEN MOLE RATIO FATTY ACID CONCENTRATIONS AND HB AND HV UNIT IN PHBHV.

Sample	Sv/(Sv+Sb)	HB unit (mole %)	HV unit (mole %)
PHB	0	100	0
PHBHV-I	0.5	76	24
PHBHV-II	0.66	65	35
PHBHV-III	0.75	62	38

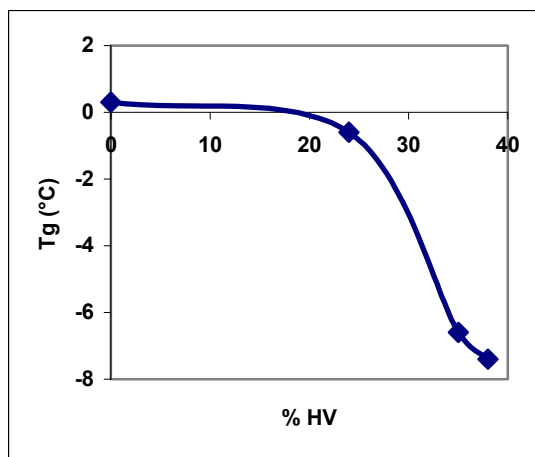


FIG. 1. DEPENDENCE OF Tg WITH %HV UNITS IN THE COPOLYMER.

The copolymer displayed typical behavior of semicrystalline polymers. At low temperature the amorphous part of the polymer is in the glassy state, and the modulus slightly increase. The storage modulus decreases in

the range -10° C at 35° C, and was roughly constant. In the range of -10° C to -2° C occur the called α transition, which is strongly related with the glass transition of the samples. In all samples, in the range of -20° C to -10° C we can observed the β transition, previously reported by others authors⁵ and characteristic of PHBHV.

TABLE II. DSC AND RX RESULTS FOR THE SAMPLES.

Sample	%HV	Tf1 (°C)	Tf2(°C)	$\Delta H_f(1)$ (J/g)	χ (%)
PHB	0	-	-	767	76
PHBHV-I	24	98.4	167.7	388	75
PHBHV-II	35	74.8	170.2	261	60
PHBHV-III	38	74.0	169.0	340	61

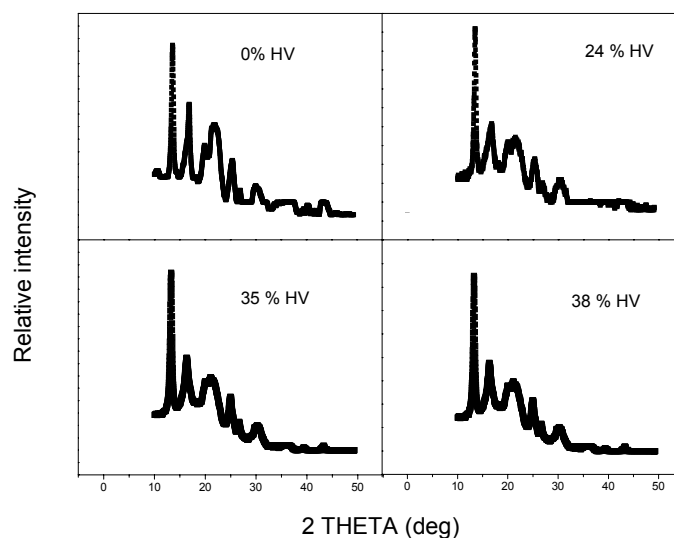


FIG. 2. WAXS SPECTRA FOR PHB AND PHBHV COPOLYMERS.

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