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Introduction. Polyhydroxyalkanoates are natural polyesters with biodegradable properties. Blending polymers is a recurrent practice to reduce costs. PHBHV with different proportions of HV units has been blended with synthetic polymers as polymethylmethacrylate (PMMA) looking for the improvement of a particular property¹. It has been reported that the blend of PHBHV with methacrylates can result in miscible systems, but not in the total window. DSC, X rays and FT-IR are useful techniques to determine the miscibility of polymeric blends².

The aim of this work is to obtain biodegradable binary blends of poly(glycidyl methacrylate) PGMA or poly(N,N-dimethylaminethylmethacrylate) PNNDMAEM (high and low molecular weight) and PHBHV with different %HV in the copolymer.

Materials and methods

Materials. Bacterial copolymer PHBHV was synthesized by fermentation using *Ralstonia eutropha* (ATCC 17699) as previously reported². N,N-dimethylaminethylmethacrylate (NNDMAEM) and glycidyl methacrylate (GMA) were purified by distillation previously to their free-radical polymerization over calcium hydride at reduced pressure. The polymerizations were carried out at 70°C for 18 h under nitrogen atmosphere.

Characterization of polymers. Elemental composition (carbon, oxygen, and hydrogen) was done for polymers (EA 110 CE Instruments Inc.). Approximately 2 mg of each material were used for their analysis. Synthesized polymers were also characterized by FT-IR spectroscopy (Perkin Elmer 2000). The increase of the refractive index as a function of concentration (dn/dc) was measured at 298 K using a Brice Phoenix 2000 differential refractometer fitted

with a neon laser beam using the same solvent at a fixed wavelength ($\lambda = 632$ nm). Light scattering measurements were used to determine the molecular weights and the classical Zimm plots used.

Blend preparation. Blends were prepared by slowly casting films from chloroform. The composition of the samples was explored in a range of 20-80 % PNNDMH (high molecular weight: A, D, G, and F series) and PNNDML (low molecular weight: B, E, H and K series) or PGMA (C, F, I and L) on PHBHV

Physical characterization of blends

DSC. The thermal behavior of the polymers was determined by a 951 TA-DSC module linked to a Thermal Analyzer 2100 microprocessor, at a heating rate of 10 °C/min under flowing nitrogen or air (flow rate = 50 mL/min). The first run was carried out from -50 to 200 °C to determine melting temperature. Tg values were obtained through a second run in the same temperature range.

X-Rays. The x-ray analysis was performed by using a horizontal goniometer (Philips 1138) coupled with a generator of a high stability (Philips 1160) and associated electronics using films of 2 x 1 cm.

Dynamic mechanical analysis. Storage modulus (G') and loss modulus (G'') were evaluated on the films. The tension films test were performed at 1 Hz. The range of temperatures tested were of -50° C to 200° C (TA instruments) with a ramp of 10 C min⁻¹.

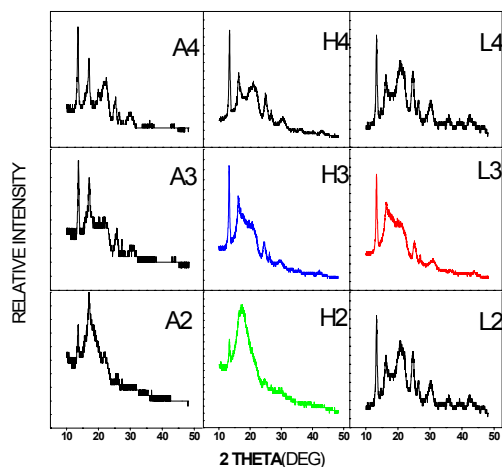
Results and Discussion.

PGMA and PNNDM (high and low molecular weight) were characterized by DSC and their Tg (°C) was 11.8, 17.4 and 15, respectively. They were amorphous. Their molecular weight were: 96,000, 105,000 and 5,000 Da, respectively.

Table 1. DSC and WASX results for the blends

Sample	% HV	Synthetic polymer	% PHBHV	Tg (°C)	χ (%)
PHB	0	---	---	0.3	76
A2	0	PNNDMH	20	-3.1	40
A3	0	PNNDMH	50	-3.9	53
A4	0	PNNDMH	80	-5.3	70
B2-B4	0	PNNDML	20-80	-3	78
C2-C4	0	PGEMA	20-80	-4	53
PHBHV I	24	---	100	-0.6	75
D2-D4	24	PNNDMH	20-80	-1	53
E2	24	PNNDML	20	-2.4	43
E3-E4	24	PNNDML	50-80	-1	71
F2-F4	24	PGMA	20-80	-2.5	41
PHBHV II	35	---	100	-6.6	60
G2-G4	35	PNNDMH	20-80	-5	49
H2-H4	35	PNNDML	20-80	-4.5	36
I2-I4	35	PGMA	20-80	-6	47
PBHV III	38	---	100	-7.4	57
J2	38	PNNDMH	20	-5.2	18
J3	38	PNNDMH	50	-4	35
J4	38	PNNDMH	80	-5.5	16
K2-K4	38	PNNDML	20-80	-6	18
L2	38	PGMA	20	-6.5	29
L3	38	PGMA	50	-6.1	36
L4	38	PGMA	80	-5.8	47

DSC and WAXS results for the blends are shown in Table I. %HV in the PHBHV copolymer is an important variable for these systems to be miscible. So that if %HV is high (H,I,J,K,I and L series) the Tg and the crystallinity degree (% χ) change when they are compared to pure PHBHV. This is an evidence of miscibility in these systems³.

**Figure 1. WAXS diffractogram for A, H and L series.**

The degree of crystallinity was determined using the the diffractograms as those shown

in Fig. 1 which correspond to three (A, H and L) of the twelve studied series. The Tg values reported correspond to the biological polymers (Table 1).

When we were looking for a second Tg, in the majority of the cases it was not possible due to the weak signal from the synthetic polymer in contrast with the sharp step from the biological polymer. The weak signal was independent of the content of PHBHV in the sample.

DMA testing did not show significant differences between blends and pure materials (PNNDMH, PHB-35%HV; G series). The results of the blends of PGMA with PHB-38%HV and PGMA PHB-35%HV-PGMA (I series), were also similar. The highest value of G' was around 2500 MPa. This value was higher than those of pure samples. When PHB-38%HV was blended with PNNDML (K series) the results showed a light increase in the G', suggesting a partial miscibility. This result is consistent with the values obtained through DSC. We can observe that PHB-38%HV is miscible with PGMA (L series) in the tested compositions. All samples showed the typical transition behaviours α γ β at Tan δ .

Biocompatibility and biodegradability are influenced by the morphology of the blend, therefore, it is recommendable to study it. At present, our group is working on these aspects.

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