Preparation of Biodegradable PHBV and Lignosulfonate Composite by Reactive Extrusion and Their Mechanical and Morphological Characterization

Lemes, A.P.¹; Soto-Oviedo, A.M.¹; Mei, L.H.I.²; <u>Durán, N.^{1,3}</u>

¹ Instituto de Química, Unicamp, C. Postal 6154, 13084-971, Campinas, SP, Brasil.

² Faculdade de Engenharia Química, Unicamp, Campinas, SP, Brasil.

³ Núcleo de Ciências Ambientais-NCA, Universidade de Mogi das Cruzes, Mogi das Cruzes, SP, Brasil.

Statement of Purpose: Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV), a copolymer of microbial polyester, and its composites are biodegradable and biocampatible, making them attractive as biomaterials for applications in both conventional medical devices and tissue engineering and for packaging materials^{1,2}.

However, the properties of filled composites depend on filler/matrix adhesion, mainly^{2,3}. Most compound processes require the addition of compatibilizers, which circumvent incompatibility problems relating to poor interfacial adhesion between filler and polymer. Many approaches have been described in the literature to improve the adhesion between organic fillers and the polymer matrix. The most prominent method is the addition of maleic anhydride polymers as compatibilizers³.

This work intended to produce a compatibilizer by grafting of maleic anhydride onto PHBV (PHBV-g-MA) in a reactive extrusion and evaluate the effect of diffeterents amounts of a compatibilizer on the mechanical and morphological properties of composites based on PHBV and lignosulfonate.

Methods: PHBV was supplied by Biocycle, which present an HV content of 15 % and weight-average molecular weight (Mw) = 235,000. The lignosulfonate Vixil-UF was supplied by Melbar Produtos de Lignina Ltda., as a brown powder with and weight-average molecular weight (Mw) = 7,700. Both materials were used as received. Composites PHBV/PHBV-g-MA/Vixil-UF containing 80 wt % PHBV and 20 wt % lignosulfonate with 0, 1.5 and 3.0 wt % maleic anhydride (MA), were prepared in a twin-screw extruder at a processing temperature 150-165°C and screw speed of 100 rpm. The grafting of maleic anhydride onto PHBV occurred during the preparation of composites in presence of dicumyl peroxide as initiator. The composites (granules) were injection-molded into test bars of 130 x 40 x 2 mm on Arburg 221K injection molding machine. Tensile strength measurements, Young's modulus and elongation at break were determined on EMIC DL 2000 equipment following ASTM D 638-95. The morphology of the composites was studied by scanning electron microscopy (SEM) in a Jeol JSM-T3000 microscope operating at 20 kV. The samples for morphology study were prepared by cryogenic fracture in liquid nitrogen. The fracture surfaces of the samples were sputtered with Pd/Au alloy in a Balzer MED 020 machine.

Results / **Discussion:** The mechanical properties of composites produced are showed in table 1. Table 1 shows an increase around 125% in yield stress values and 145% in elongation at break values in the composites with addition of maleic anhydride. This result indicate that a

compatibilizer was produced during the extrusion and it improves mechanical properties of composites. The values of yield stress and elongation at break are the same for the composites containing different amounts of maleic anhydride.

Table 1: Mechanical Properties of PHBV/PHBV-*g*-MA/Vixil-UF composites with different addition of maleic anhydride.

MA (%)	Yield Stress (MPa)	Elongation at break (%)	E (MPa)
0	13.6 ± 4.0	1.7 ± 0.4	1954 ± 498
1.5	31.5 ± 2.0	4.2 ± 0.4	2211 ± 247
3.0	27.7 ± 1.3	3.2 ± 0.4	1945 ± 319

Scanning electron micrographs of fractured surfaces of the composites with and without maleic anhydride are shown in Figure 1. It was observed the absence of any physical contact between lignosulfonate and PHBV in the Figure 1A, indicating that the interfacial adhesion between filler and matrix is poor. However, in the composite that contain maleic anhydride, a decrease of phase segregation between the components is observed. Then, the micrographs revealed that maleic anhydride addition improved morphological properties of the composites.



Figure 1. Micrographs of fracture surface of PHBV/PHBV-g-MA/Vixil-UF composites with 0 wt % (A) and 1.5 wt % (B) of maleic anhydride

Conclusions: Results show that addition of maleic anhydride on the composites improved the morphology and mechanical properties of composites. This improvement can be attribued to the production of a compatibilizer, maleic anhydride grafted PHBV (PHBV-*g*-MA), during the composites preparation.

References:

1. Chen G-Q. and Wu Q. Biomaterials. 2005;26:6565-6578.

2. Dufresne A., Dupeyre D., Paillet M. J. Appl. Polym. Sci. 2003;87:1302-1315.

3. Nitz H., Semke H., Landers R., Mülhaupt R. J. Appl. Polym. Sci. 2001;81:1972-1984.