Mechanical and Morphological Properties of Poly(3-hydroxybutyrate)/ Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) Blends

Denise Santos Conti,[1] *Sérgio Henrique Pezzin,*[2] *Luiz Antônio Ferreira Coelho**[2]

Summary: With the objective of developing new biodegradable materials, the mechanical properties and the morphology of blends of poly(3-hydroxybutyrate), P(3HB), and poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate), P(3HB-*co*-3HV), were studied in this work. P(3HB) (492 $kg \cdot mol^{-1}$)/P(3HB-*co*-3HV)-6%3HV (294.2 $kg \cdot mol^{-1}$) blends were prepared by injection in a wide range of proportions and characterized by mechanical behavior of tensile strength, Izod impact strength and hardness Shore D. According to the increase of the copolymer content in the blend, it was detected that the hardness Shore D and the maximum tensile strength presented a significant reduction, the elasticity modulus showed a significant reduction, the elongation at break presented a significant increase and the Izod impact strength practically remained constant. Scanning electronic microscopy (SEM) was carried out in the fractured surface of the samples obtained during the tests of tensile and impact strength. These analyses showed a morphology with fragile fracture for whole blends, agreeing with mechanical results previously reported.

Keywords: blends; mechanical properties; poly(3-hydroxybutyrate); poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate); SEM

Introduction

Diverse studies have been made on biodegradable polymers aiming to make viable the use of these materials in daily applications with the objective to minimize impacts caused in the environment,.[2,3,6,7,20]

Polyhydroxyalkanoates (PHAs) are a class of naturally occurring biodegradable and biocompatible polyesters that are produced by a wide variety of different microorganisms.[11,12] Since the conventional synthetic polymers have the disadvantage of low microbial decomposition rate and the lifetime of hundreds of years when discarded in to the environment, the PHAs have been receiving keen interest, among all natural biodegradable polymers, due to its mechanical properties similar to those of synthetic polymers.[2,13]

Poly(3-hydroxybutyrate), P(3HB), discovered by Lemoigne in 1925, is one of the most studied bacterial polyesters in the PHA family.[9,14,15,18] P(3HB) is one of the most studied biopolymers, mainly its use in blends with other polymers in function of its high rigidity and difficulty of processing. This polymer is a highly crystalline thermoplastic with a relatively high melting temperature (170–180 °C) and a glass transition temperature in the range from 0 to 5 °C. Mechanically, P(3HB) is a brittle material with a large elastic modulus and high tensile strength.[9,14,19]

Another important biopolymer is the poly(3-hydroxybutyrate-*co*-3-hydroxyvale-

[1] Sociedade Educacional de Santa Catarina - SOCIESC, Escola Técnica Tupy - ETT, Department of Materials, Rua Albano Schmidt n.3333, Bairro Boa Vista, ZIP CODE 89227-700, Joinville, SC, Brazil
[2] Universidade Estadual de Santa Catarina - UDESC, Centro de Ciências Tecnológicas - CCT, Campus Universitário Prof. Avelino Marcante s/n, Bairro Bom Retiro, ZIP CODE 89223-100, Joinville, SC, Brazil
Tel.: 55+47+3431-7335; Fax.: 55+47+3431-7240
E-mail: lcoelho@joinville.udesc.com.br

rate), P(3HB-*co*-3HV), released by ICI in 1983 as Biopol®.[16] This copolymer is more ductile and flexible than P(3HB) due to the presence of units of 3-hydroxyvalerate (3HV) in its molecular structure, whose molar content can change.[1,2] The increase of the 3HV content in the copolymer reduces the melting temperature, the crystallinity, the modulus of elasticity and the tensile strength, but increases the flexibility, the impact strength and the ductility.[1,2] However, P(3HB-*co*-3HV) with low 3HV content (less than 15 mol%) is quite fragile.[8] Nevertheless, P(3HB) and P(3HB-*co*-3HV) are promising candidates to be widely applied in many areas, including medicine, pharmacology, packaging and agriculture.[9,10]

Blending of polymers is an effective way to acquire new materials with desired properties. There are many references attempting to blend P(3HB) with other polymers, with the aim of improving its mechanical properties and its utility in daily applications.[16,20] However, blends of P(3HB) and P(3HB-*co*-3HV) have been barely studied in the literature. In this way these work is focused in the mechanical and morphological properties of the P(3HB)/P(3HB-*co*-3HV)-6%3HV blends processed by injection.

Experimental

Sample Preparation

The biopolymers were supplied by PHB Industrial (Brazil) with the trade name Biocycle®, in the form of a white fine powder. The specifications are summarized in Table 1.

These materials were mixed manually in 100/0, 80/20, 50/50, 20/80 and 0/100 P(3HB)/P(3HB-*co*-3HV)-6%3HV (w/w) ratios, and kept in oven with air circulation at 45 °C for 24 hours. Samples for mechanical tests of tensile strength (ISO 527 norm) and Izod impact strength (ISO 180 norm) were injected in a Sandretto Injection Machine. The moulds of injection machine were kept around 26 °C. The injection parameters were regulated according to recommendations of the supplier and fitted for necessary minimum values to obtain the samples for the mechanical tests. The samples were kept at 23 °C (±2 °C) and 50% (±5 °C) of relative humidity at least 48 hours before the tests.

Table 1.
Specification of biopolymers.

Biopolymer	3HV content (% molar)	Molar mass (Mw) ($kg \cdot mol^{-1}$)
P(3HB)	0	492.0
P(3HB-co-3HV)	6	294.2

Mechanical Properties

The tests of tensile strength were carried out in a Kratos Universal Machine, with load cell of 500 Kgf and speed of 5 $mm \cdot min^{-1}$. The modulus of elasticity was determined in an Emic Universal Machine with strain gauge TRD6, load cell of 100 Kgf and speed of 5 $mm \cdot min^{-1}$. The tests of Izod impact strength were carried out in a EMIC AIC-1-1984 Machine with pendulum of 2.7 Joules The hardness Shore D was evaluated in accordance with ASTM D2240 norm, using the plane surface of the samples employed in the tensile strength test, in an equipment Woltest SD300, weight of 5 kg and penetration time of 14 seconds.

Morphological Analyses

The fractured surface of the samples during the tensile and the impact strength tests were metallized with gold layer in Baltec SCD050 Machine and analyzed in Scanning Electronic Microscope Zeiss DSM 940A, with voltage of 5 or 10 kV and current of 80 mA.

Results and Discussion

Mechanical Properties

Table 2 shows the results of the mechanical properties of P(3HB)/P(3HB-*co*-3HV)-6%3HV blends.

Table 2.
Mechanical properties of P(3HB)/P(3HB-*co*-3HV)-6%3HV blends.

Composition	Tensile strength (MPa)	Elongation at break (%)	Modulus of elasticity (GPa)	Izod impact strength ($J \cdot m^{-1}$)	Hardness Shore D
100/0	26.0 (±2.6)	8.2 (±0.4)	4.6 (±1.1)	47.8 (±3.6)	72.4 (±1.0)
80/20	21.5 (±3.6)	10.4 (±0.5)	3.9 (±1.6)	48.9 (±3.3)	71.1 (±0.6)
50/50	23.6 (±1.0)	10.6 (±0.4)	3.5 (±0.4)	51.1 (±3.3)	71.1 (±0.9)
20/80	25.3 (±0.7)	9.1 (±0.4)	3.0 (±0.3)	48.7 (±2.5)	70.2 (±1.3)
0/100	21.8 (±1.5)	12.1 (±0.9)	2.7 (±0.1)	51.0 (±6.1)	68.9 (±1.2)

The Force *versus* the Deformation curves of the pure biopolymers and blends showed typical behavior of fragile material, that is, the samples broke soon after the proportinality limit, without any deformation which could be related to tenacity.

It was verified that the tensile strenght of the P(3HB) overcame in 16.1% the tensile strenght of the P(3HB-*co*-3HV)-6%3HV (Table 2 and Figure 1). Similar results for P(3HB) obtained by injection were found by Medeiros et al.[21] (24,5 MPa) and Rosa et al.[17] (25,0 MPa). For the injected P(3HB-*co*-3HV)-6%3HV results determined by Bhardwaj et al.,[22] showed 26 MPa for P(3HB-*co*-3HV)-13%3HV.

The inferior tensile strenght of the P(3HB-*co*-3HV)-6%3HV in relation to the P(3HB) occurred due to 3HV 6 mol% content in the molecular structure of the copolymer. The presence of etil group in the units 3HV it becomes difficult the crystallization process, producing a polymer less crystalline and with less perfect cristals, that contributes for the reduction of the tensile strenght.

In general, the tensile strength of blends was inferior to the P(3HB) pure: 17.3%, 9.2% and 2.7% for 80/20, 50/50 and 20/80 blends, respectively. It was expected that the increase of the copolymer content in the blends could produce materials with lesser tensile strength as observed by Barham and Organ.[3] These authors obtained reduction of the tensile strength according to the increase of the 3HV molar content in blends P(3HB)/P(3HB-*co*-3HV)-18,4%3HV and P(3HB)/P(3HB-*co*-3HV)-19,7%3HV produced by compression. However, the increase of tensile strength in the 50/50 and 20/80 blends in relation to 80/20 blend can be associated to processing conditions, since the 50/50 and 20/80 blends were injected with hold pressure higher than 80/20 blend.[4,5]

Related to the elongation at break (Table 2 and Figure 2), it was observed that the P(3HB-*co*-3HV)-6%3HV showed

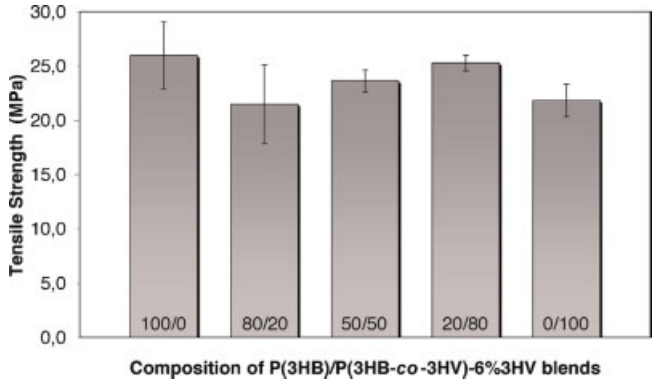

Figure 1.
Tensile strength of P(3HB)/P(3HB-*co*-3HV)-6%3HV blends obtained by injection.

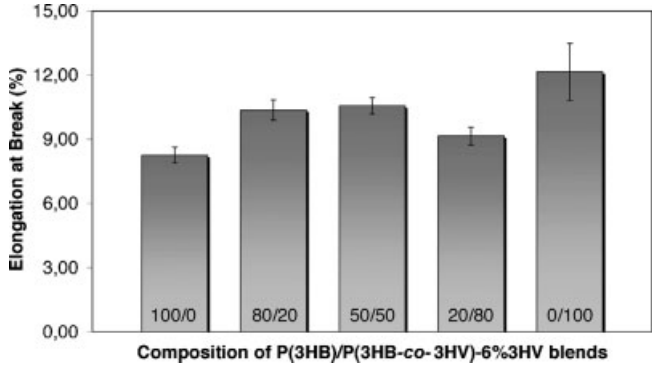

Figure 2.
Elongation at break of P(3HB)/P(3HB-*co*-3HV)-6%3HV blends obtained by injection.

this property higher than P(3HB). As commented previously, this slightly superior flexibility of the copolymer is related to the 6 mol% of 3HV in the molecular structure Ramsay et al.[23] determined 17,7% as elongation at break for P(3HB-*co*-3HV)-19,1%3HV molded by compression. Similar results of elongation at break for P(3HB) were determined by Brassilious[14] and El-Hadi et al.,[16] about 10% for P(3HB) molded by compression.

The 80/20, 50/50 and 20/80 blends presented elongation at break higher than P(3HB), suggesting that the increase of the copolymer content in the blend provides the molecular mobility, resulting in a material more flexible and with better capacity of deformation. Barham and Organ[3] verified the increase of the elongation according to the increase of the 3HV molar content in blends P(3HB)/P(3HB-*co*-3HV)-18,4%3HV and P(3HB)/P(3HB-*co*-3HV)-19,7%3HV molded by compression. However, the little increase of this property in 50/50 blend and the reduction in 20/80 blend, in relation to 80/20 blend, also can be associated to the processing conditions as already pointed out previously.

The modulus of elasticity of the pure biopolymers and the P(3HB)/P(3HB-*co*-3HV)-6%3HV blends is presented in Table 2 and Figure 3. These results showed that the increase of the copolymer content diminished the modulus of elasticity significantly. The reduction is about 15.9% for 80/20 blend, 24.5% for 50/50 blend, 34.4% for 20/80 blend and 41.7% for the pure

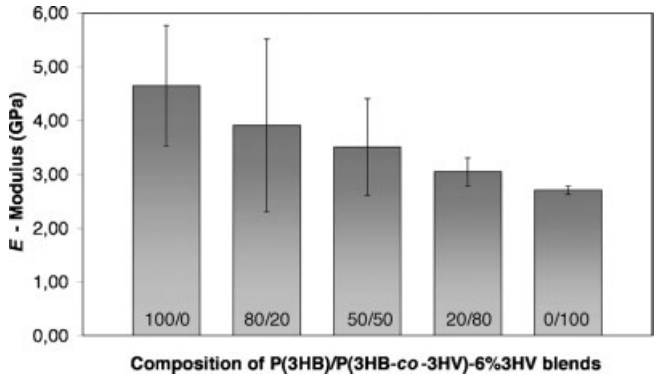

Figure 3.
Modulus of elasticity of P(3HB)/P(3HB-*co*-3HV)-6%3HV blends obtained by injection.

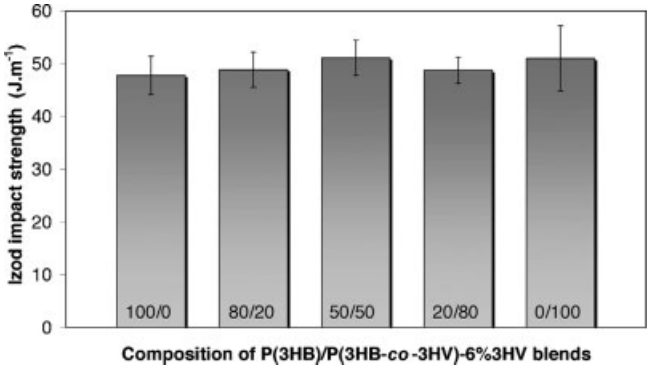

Figure 4.
Izod impact strength of P(3HB)/P(3HB-*co*-3HV)-6%3HV blends obtained by injection.

P(3HB-*co*-3HV)-6%3HV, in relation to the P(3HB). This behavior suggests that the 3HV 6 mol% content in the copolymer resulted in lesser rigidity. Similar results of reduction of modulus of elasticity according to the increase of the 3HV molar content was observed by Barham and Organ[3] in P(3HB)/P(3HB-*co*-3HV)-18,4%3HV and P(3HB)/P(3HB-*co*-3HV)-19,7%3HV blends molded by compression.

As one can see in the Table 2 and Figure 4, the increase of the P(3HB-*co*-3HV)-6%3HV content practically did not modify the Izod impact strength of the blends in relation to the P(3HB). A little significant rise of 2.3% for 80/20 blend, 7.0% for 50/50 blend, 2.0% for 20/80 blend and 6.7% for the P(3HB-*co*-3HV)-6%3HV was obtained. Such behavior is due to low 3HV molar content presents in the copolymer (only 6%). These results agree to the lack of tenacity these blends that was observed by curves Force *versus* Deformation and by the results obtained for tensile strength and elongation at break. Moreover, the difficult conditions of processing during the samples injection also can have influenced these results, therefore Brydson[1] presents the Izod impact strength for P(3HB) in 30 $J \cdot m^{-1}$ and about 90 $J \cdot m^{-1}$ for P(3HB-*co*-3HV)-6%3HV.

It was not observed significant differences in the superficial hardness of blends according to the increase of the P(3HB-*co*-3HV)-6%3HV content, only a light reduction in relation to the P(3HB): 1.8% for 80/20 and 50/50 blend, 3.04% for 20/80 blend and 4.83% for the P(3HB-*co*-3HV)-6%3HV. Such behavior is associated with the low content of 3HV in the copolymer,

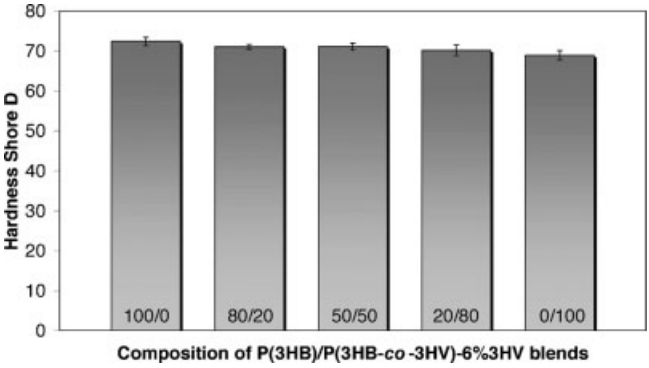

Figure 5.
Hardness Shore D of P(3HB)/P(3HB-*co*-3HV)-6%3HV blends obtained by injection.

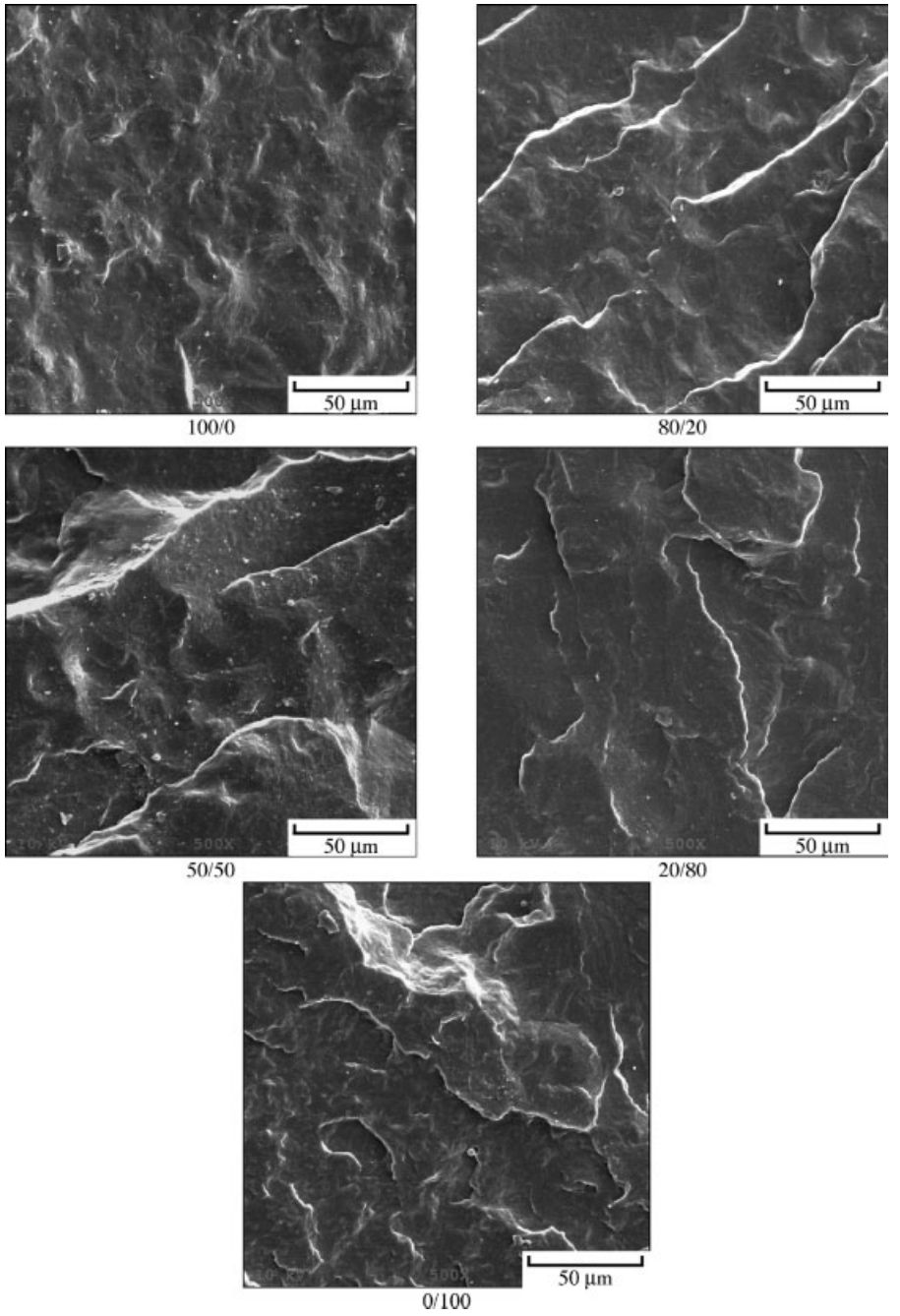

Figure 6.
SEM of fracture surface of the Izod impact samples of P(3HB)/P(3HB-*co*-3HV)-6%3HV blends (500×).

that is only 6 mol%. Saha et al.[24] has obtained 51 units hardness Shore D for P(3HB-*co*-3HV)-19%3HV and Duarte[6] found 71.3 units hardness Shore D for P(3HB).

Morphological Analyses

SEM analyses showed a fragile morphology for blends and pure biopolymers. The increase of P(3HB-*co*-3HV)-6%3HV con-

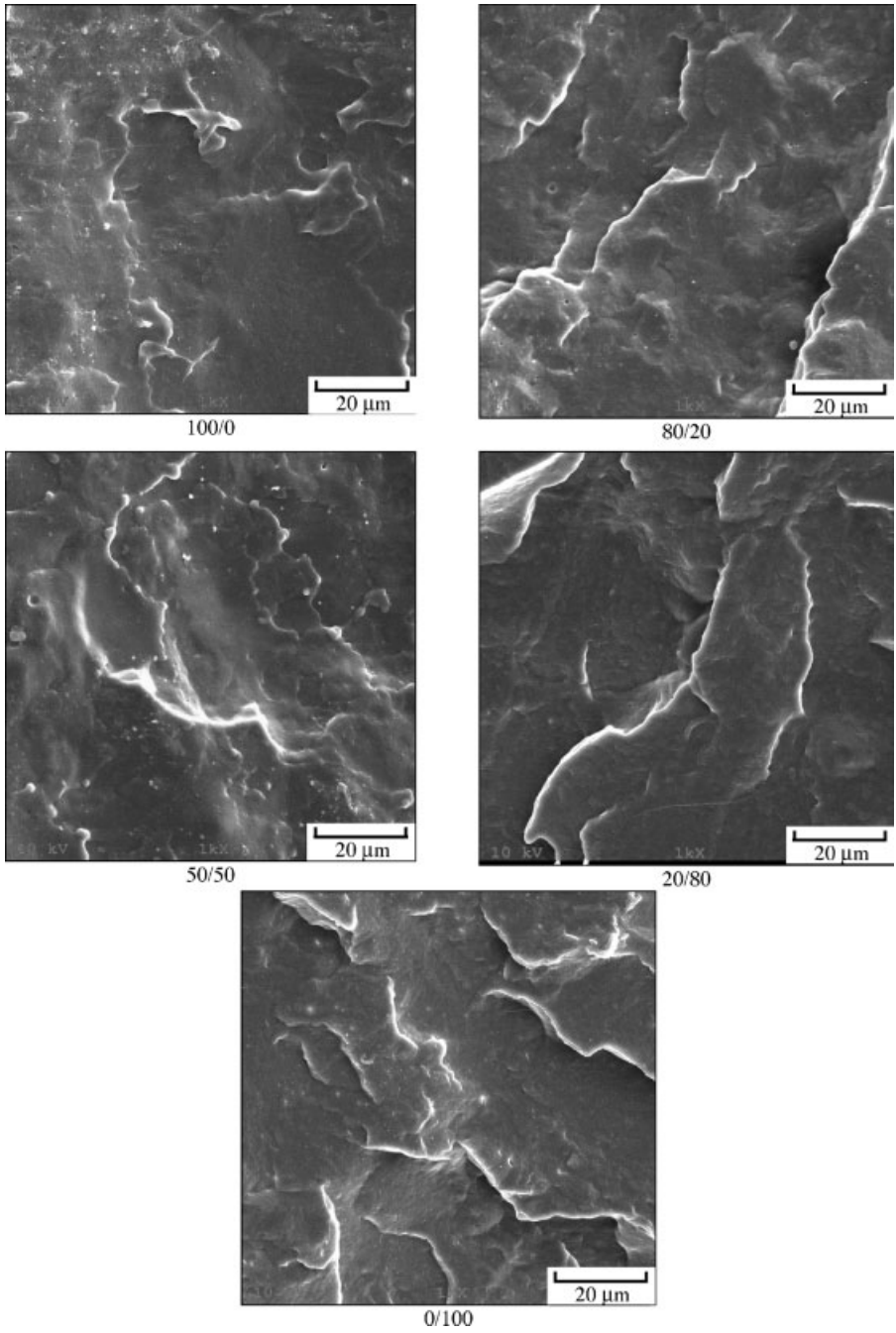

Figure 7.
SEM of fracture surface of the Izod impact samples of P(3HB)/P(3HB-*co*-3HV)-6%3HV blends (1000×).

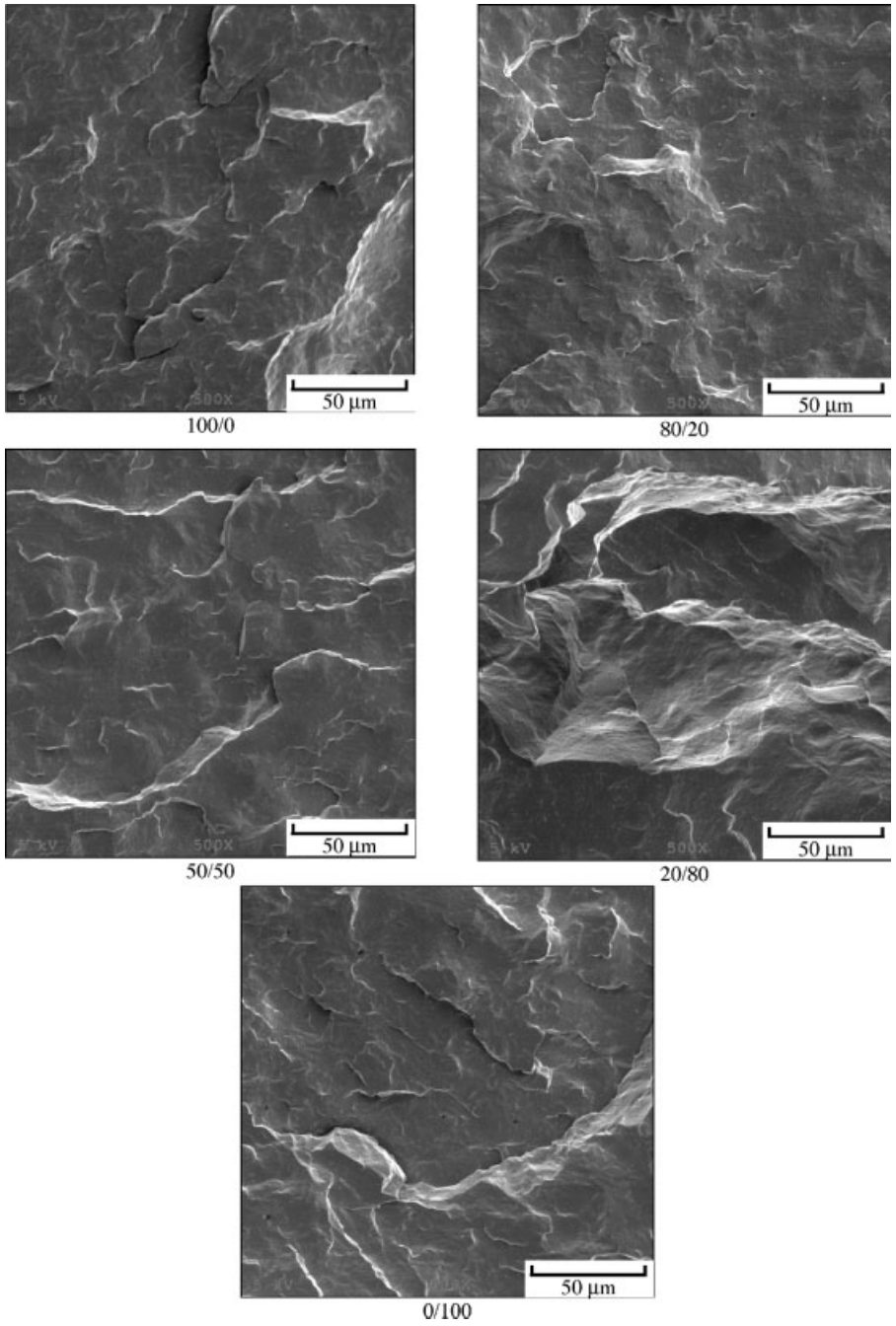

Figure 8.
SEM of fracture surface of the tensile strength samples of P(3HB)/P(3HB-*co*-3HV)-6%3HV blends (500×).

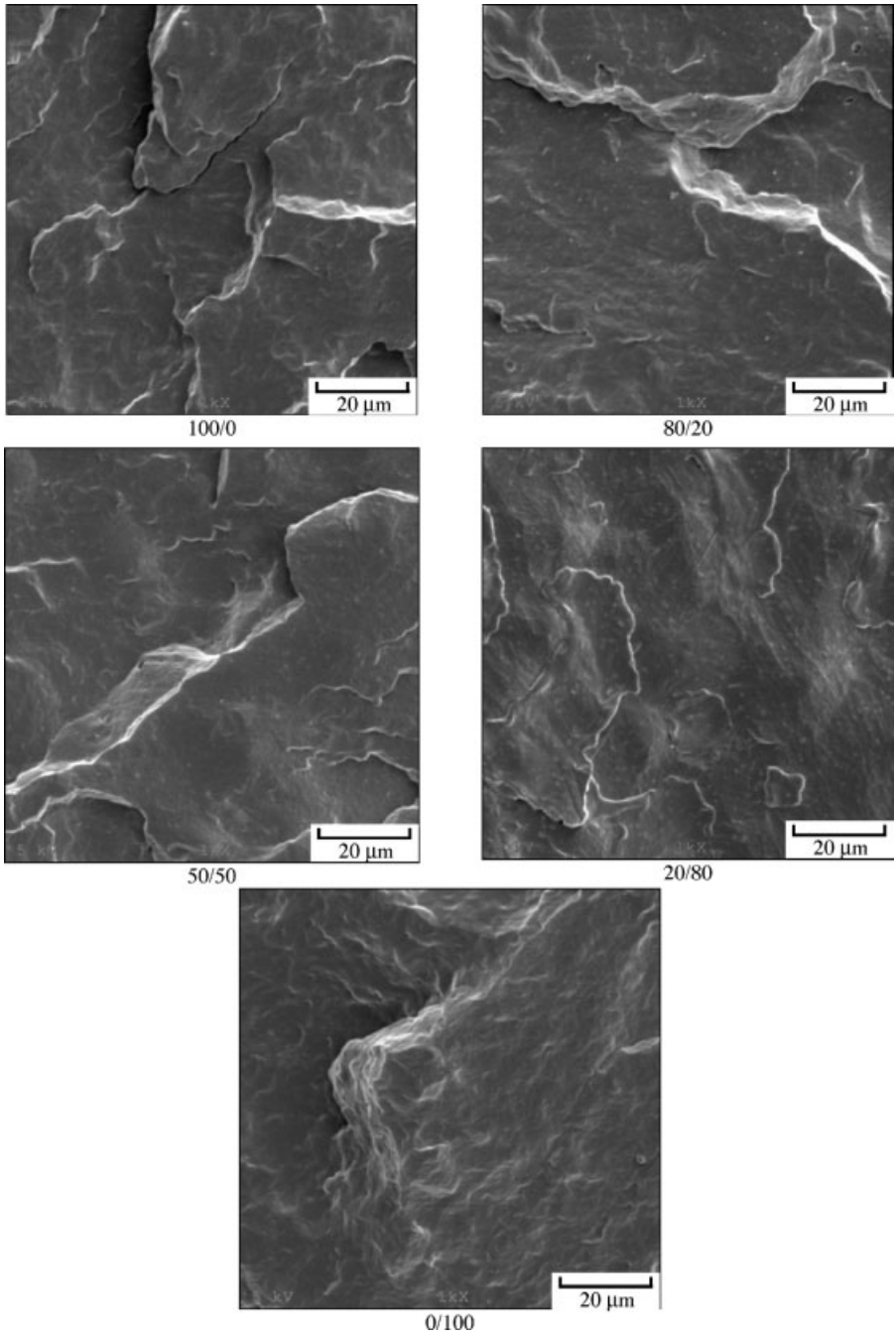

Figure 9.
SEM of fracture surface of the tensile strength samples of P(3HB)/P(3HB-*co*-3HV)-6%3HV blends (1000×).

tent in the blends was not enough to produce a ductile morphology (Figures 6, 7, 8 and 9). The fractures occurred by regular propagation and in layer stratified, characterizing the fracture fragile. This behavior agreed with mechanical results reported. Phase separation was not observed, that suggests a good homogenization between the components.

Conclusions

The mechanical behavior of P(3HB)/P(3HB-*co*-3HV)-6%3HV blends were modified according to the copolymer content. The higher P(3HB-*co*-3HV)-6%3HV content in the blend produced a more flexible material, since it was obtained a reduction in the hardness and tensile strength, a increase in the elongation at break, and the Izdo impacto strength remained practically constant. The modulus of elasticity reduced significantly according to the higher copolymer content in blends. These results indicated that the increase of the amount of 3HV in the blend by copolymer increases molecular mobility and produces a more flexible material. By SEM, it was observed that pure biopolymers and blends presented fragile morphology, since the fractures occurred by regular propagation in stratified layers. This behavior was obtained since the 3HV content in the copolymer was only 6 mol%, that is, the 3HV content in the blends was not enough to produce a ductile material.

Acknowledgements: The authors thank the PHB Industrial SA (Brazil) for the supply of the biopolymers and CAPES for financial support.

[1] J. A. Brydson, "*Plastics Materials*", 7th.ed., Butterworth Heinemann, Oxford **2000**.
[2] D. S. Rosa, R. Pantano Filho, "Biodegradação: um ensaio com polímeros", Moara, Itatiba; Universidade São Francisco, Bragança Paulista **2003**.
[3] P. J. Barham, S. J. Organ, *Journal of Materials Science* **1994**, *29*, 1676.
[4] R. W. Holdschmidt, "*Injeção Técnica*", Promold S/C Ltda, Curitiba **2001**.
[5] P. Thienel, "IX Simpósio sobre Tecnologia de Plásticos Brasil-Alemanha", São Paulo **1997**.
[6] M. A. T. Duarte, "Dissertação de Mestrado", Universidade do Estado de Santa Catarina, Joinville **2004**.
[7] M. Avella, E. Martusceli, M. Raimo, *Journal of Materials Science* **2000**, *35*, 523.
[8] B. Fei, C. Chen, H. Wu, S. Peng, X. Wang, L. Dong, *European Polymer Journal* **2003**, *39*, 1939.
[9] L. M. W. K. Gunaratne, R. A. Shanks, G. Amarasinghe, *Thermochimica Acta* **2004**, *423*, 127.
[10] T. Volova, E. Shishatskaya, V. Sevastianov, S. Efremov, O. Mogilnaya, *Biochemical Engineering Journal* **2003**, *16*, 125.
[11] A. J. Anderson, E. A. Dawes, *Microbiol. Rev.* **1990**, *54*, 450.
[12] A. Steinbüchel, *Macromol. Biosci.* **2001**, *N1*, 1.
[13] Y. Doi, "*Microbial Polyesters*", VCH Publishers, New York **1990**.
[14] D. Briassoulis, *Journal of Polymers and the Environment* **2004**, *12*, 65.
[15] A. Padermshoke, Y. Katsumoto, H. Sato, S. Ekgasit, I. Noda, Y. Ozaki, *Spectrochimica Acta Part A* **2005**, *61*, 541.
[16] A. El-Hadi, R. Schanabel, E. Straube, G. Muller, S. Henning, *Polymer Testing* **2002**, *21*, 665.
[17] D. S. Rosa, N. T. Lotto, D. R. Lopes, C. G. F. Guedes, *Polymer Testing* **2004**, *23*, 3.
[18] S. Iannace, L. Ambrosio, S. J. Huang, L. Nicolais, *Journal of Applied Polymer Science* **1994**, *54*, 1525.
[19] L. Zhang, C. Xiong, X. Deng, *Polymer* **1996**, *37*, 235.
[20] C. C. Han, J. Ismail, H. W. Kammer, *Polymer Degradation and Stability* **2004**, *85*, 947.
[21] I. L. Medeiros, J. M. S. A. Maracacini, M. A. T. Duarte, S. H. Pezzin, J. C. Sobral, P. S. Balzer, H. P. Bernardo, M. T. Everling, A. P. T. Pezzin, *Revista Matéria* **2005**, *10*, 465.
[22] R. Bhardwaj, A. K. Mohanty, L. T. Drzal, F. Pourboghrat, M. Misra, *Biomacromolecules* **2006**, *7*, 2044.
[23] B. A. Ramsay, V. Langlade, P. J. Carreu, J. A. Ramsay, *Applied and Environmental Microbiology* **1993**, *59*, 1242.
[24] S. P. Saha, A. Patra, A. K. Paul, *J. Ind. Microbiol. Biotechnol.* **2006**, *33*, 377.

