# Properties of Melt-processed Poly(hydroxybutyrate-co-hydroxyvalerate)/starch 1:1 Blend Nanocomposites

**Natália F. Magalhães, Cristina T. Andrade**
*Instituto de Macromoléculas Professora Eloisa Mano, UFRJ*

**Abstract:** Melt blending of 1:1 poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and glycerol-plasticized starch (TPS) was performed in the presence of an organically-modified montmorillonite, incorporated at 2.5, 5, 7.5 and 10 wt% amounts. Scanning electron micrographs (SEM) revealed the role of the organoclay as a compatibilizing agent for the immiscible blend. The blends were also characterized by X-ray diffraction (XRD), tensile tests, humidity absorption and soil burial biodegradation tests. The results indicated improved properties of the hybrid materials in relation to TPS alone, with a faster biodegradation rate than PHBV.

**Keywords:** *Biodegradable blend, thermoplastic starch, PHBV, modified montmorillonite.*

## Introduction

Two main reasons have been addressed to justify the development of new environmentally-friendly technologies and products. The disposal of synthetic plastic waste has become a challenge for governments and a health threat to consumers. Also, the uncertain increasing prices associated with the depletion of fossil sources have contributed to attract the attention of researchers and industries to biobased products[1]. However, nowadays bioplastics share a market of less than 0.4 wt% of world plastics consumption, frequently related to cost and technical performance issues[2].

Polyhydroxyalcanoates (PHA) consist of a group of biocompatible and biodegradable aliphatic polyesters, synthesized from renewable resources by bacteria, such as *Ralstonia eutropha* and *Azobacter chroococcum*, where they are deposited as insoluble inclusions in the citoplasm. An excess of a carbon source and limiting concentrations of essential nutrients are required for their production. Poly(3-hydroxybutyrate) (PHB) and the copolymer poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) are produced commercially, but their high melting point (>170°), high crystallinity and brittleness, and a narrow processing window, hinder their practical application[3-5]. Improved properties have been achieved for PHA copolymers of 3-hydroxybutyrate and other medium-chain length 3-hydroxyalcanoate comonomers. An increase in toughness, flexibility and processability, and a reduction in crystallinity and brittleness were observed for copolymers with a relatively small amount of those comonomers[6]. To improve the properties of PHAs, composites[7-13] and polymer blends[14-33] were also studied.

For composites, an increase of 175% in the tensile modulus and of 9 °C in the heat deflection temperature in relation to the neat polymer was achieved for PHBV loaded with bamboo fiber at 40% content[9]. Cellulose nanowhiskers (CNW) with 50 nm to 500 nm in length, homogenenuously dispersed in a PHBV matrix, were shown to be effective nucleating and reinforcing agents. At 5 wt% composition, CNW contributed to increases of 77% in Young's modulus and 41% in storage modulus[10]. An organically-modified montmorillonite was also shown to act as nucleating agent for PHB[8] in the same way as silica nanospheres and nanofibers for PHBV with 7.2 mol% of hydroxyhexanoate units[5]. The addition of clay mineral nanoparticles favored the biodegradation rate of both polymers[8,13]. However, in the case of silica nanocomposites, the observed improvement in mechanical properties was reported not to be due to changes in crystallinity or spherulitic morphology[5].

Many works have been published on PHAs blends, especially with other biodegradable polymers. In general, the polymer pair is immiscible, and compatibilization constitutes the primary difficulty to be overcome. In particular, some efforts have been made to produce melt-processed PHBV/thermoplastic starch with the aim of decreasing cost and improve the biodegradation rate. In fact, the incorporation of 30 wt% of cassava starch to a 70:30 PHBV/poly(butylene adipate-*co*-terephthalate) blend led to a higher biodegradation rate without significant changes in mechanical properties[24]. For the 80:20 blend of PHBV with 5 mol% of hydroxyvalerate and high-amylose starch, improvement of compatibilization was achieved during processing with an organic peroxide[34].

Recently, some results were published concerning the role of clay minerals nanoparticules as compatibilizing and reinforcing agents for some immiscible synthetic polymer blends, when located at the interface or within the continuous phase[34-38]. Considering the favorable interactions between starch and montmorillonites[39-41], the objective of this work was to investigate the properties of 1:1 PHBV and regular cornstarch blend nanocomposites, prepared by melt-extrusion in the presence of increasing contents of an organically-modified montmorillonite.

*Corresponding author: **Cristina T. Andrade**, Instituto de Macromoléculas Professora Eloisa Mano, Centro de Tecnologia, Universidade Federal do Rio de Janeiro – UFRJ, Av. Horácio Macedo, 2030, Bloco J, CEP 21945-970, Rio de Janeiro, RJ, Brasil, e-mail: ctandrade@ima.ufrj.br*

## Experimental

### *Materials*

PHBV with 3.4 mol% hydroxyvalerate units was provided by PHB Industrial (Serrana, SP, Brazil). Regular cornstarch was supplied by Corn Products Brazil (São Paulo, SP, Brazil). Analytical grade glycerol was supplied by Vetec Química Fina (Rio de Janeiro, RJ, Brazil). Cloisite® 30B (C30B), a montmorillonite modified with dihydroxyethyl alkyl methylammonium ions, was supplied by Southern Clay Products (Gonzales, TX, USA).

### *Methods*

#### Blends preparation

Starch and 25 wt% glycerol were previously mixed in a conventional blender and kept in plastic bags at 4 ºC for 2 days. The same blender was used to homogenize 1:1 PHBV/starch and PHBV/starch/C30B mixtures. C30B was added at 2.5, 5.0, 7.5 and 10 wt% compositions, based on the total weight of the polymer components. The processings were carried out in a Coperion ZSK 18 (Werner & Pfleiderer GmbH & Co. KG, Stuttgart, Germany) co-rotating twin-screw extruder, with L/D ratio of 40, using a temperature profile of 150, 150, 155, 155, 155, 150, 150 ºC, and a screw speed set at 200 rpm. The resulting materials were compression-molded by heating at 170 ºC under $68.9 \times 10^6$ N/m² for 6 minutes, and cooling for 5 minutes in a cold press.

#### Characterization of materials

The morphology of the samples was examined with a Jeol electron microscope, model JSM-5610LV (Akishima-shi, Japan) at the acceleration voltage of 5 kV. Samples were cryogenically fractured, and vacuum-coated with gold before measurements.

X-ray diffraction (XRD) patterns were obtained at room temperature with a Miniflex diffractometer within the 2-35º (2θ) angular region, and with a Ultima IV diffractometer within the 0.6-10º (2θ) angular region, both equipments from Rigaku Corporation (Osaka, Japan). The CuKα radiation (wavelength of 1.542 Å), was generated at 30 kV and 15 mA, and at 40 kV and 20 mA, respectively. In the first case, the samples were scanned at a rate of 1°/min, and in the second case at a 0.01°/s rate.

Extruded and compression-molded films, with dimensions of 25 mm × 25 mm × 1.70 mm, were dried in an oven at 70 ºC for 72 hours. After weighing, the samples in triplicate were conditioned in a climatic chamber (M.S. Mistura, model MS 012, Rio de Janeiro, Brazil), at 25 ºC and 55% relative humidity (RH), and periodically weighed in an analytical balance (with a precision of 0.1 mg). The humidity absorption for the samples was determined in percentage according to Equation 1.

$$\text{Humidity absorption (\%)} = \frac{M_t - M_o}{M_o} \times 100 \qquad (1)$$

where $M_t$ is the weight at time t and $M_o$ is the weight of the dry material.

Tensile tests were performed with a Instron Universal Testing Machine model 4204 equipped with a 1 kN load cell, at a speed of 1 mm/min, according to ASTM D-638-03. The samples were conditioned at the same conditions of the test (21 ºC, 50% relative humidity) for 48 hours before the experiment. The average value from a total of nine measurements was taken.

Soil burial tests were carried out for the samples under laboratory conditions (average temperature of 25 ºC). The initial pH of soil was 6.5, and the final pH was 5.8. Samples were cut into pieces with 25 mm × 25 mm × 1.7 mm dimensions, weighed, and buried in a plastic container (10 L) filled with soil enriched with 30 wt% of organic materials of vegetable origin, previously passed through a 2 mm sieve. Every 15 or 30 days, for a period of 150 days, five replications of each sample were taken out of the container, cleaned with a smooth brush, and weighed. The average weight was considered. Periodically, the soil moisture content was measured; an average value of 20 wt% was maintained during the period of the test. Weight loss of the specimens with time was used to evaluate degradation.

## Results and Discussions

According to the producer, the PHBV with 3.4 mol% hydroxyvalerate units has a melting point of 172 ºC. However, melt-processing of the formulations, even PHBV alone, was possible at temperatures in the range 150-155 ºC, due to the high shearing conditions used. No antioxidant was added and, as expected, some browning was observed for the resulting extrudates, which were visually homogeneous and reasonably resistant.

The morphology of the materials fractured surfaces was visualized by SEM (Figure 1). The smooth surface of TPS (Figure 1b), which indicates that the native granular form was destroyed, contrasts with the rough PHBV morphology (Figure 1a). The processing conditions led to the complete rupture of the starch granular structure. The immiscibility between the components of the 1:1 neat blend is supported by the large size of the particularly irregular and separate smooth and rough phases (Figure 1c). With the addition of increasing amounts of C30B, changes may be observed. Not only the interfacial adhesion between PHBV and starch was increased, but the size of the particles was significantly reduced. In Figure 1g, with the addition of 10 wt% C30B, the material surface presented a uniform morphology. For other systems, such results have been attributed to the concentration of nanoparticles at the interface preventing coalescence by a barrier-type mechanism[35]. On the other hand, as reported previously, in the case of the addition of the components all together in the extruder, if one polymer melts at a temperature significantly lower than the other, the solid particles tend to be dispersed preferentially into this phase[42]. Considering that plasticized starch melts first, the C30B particles could also be located within the TPS continuous phase.
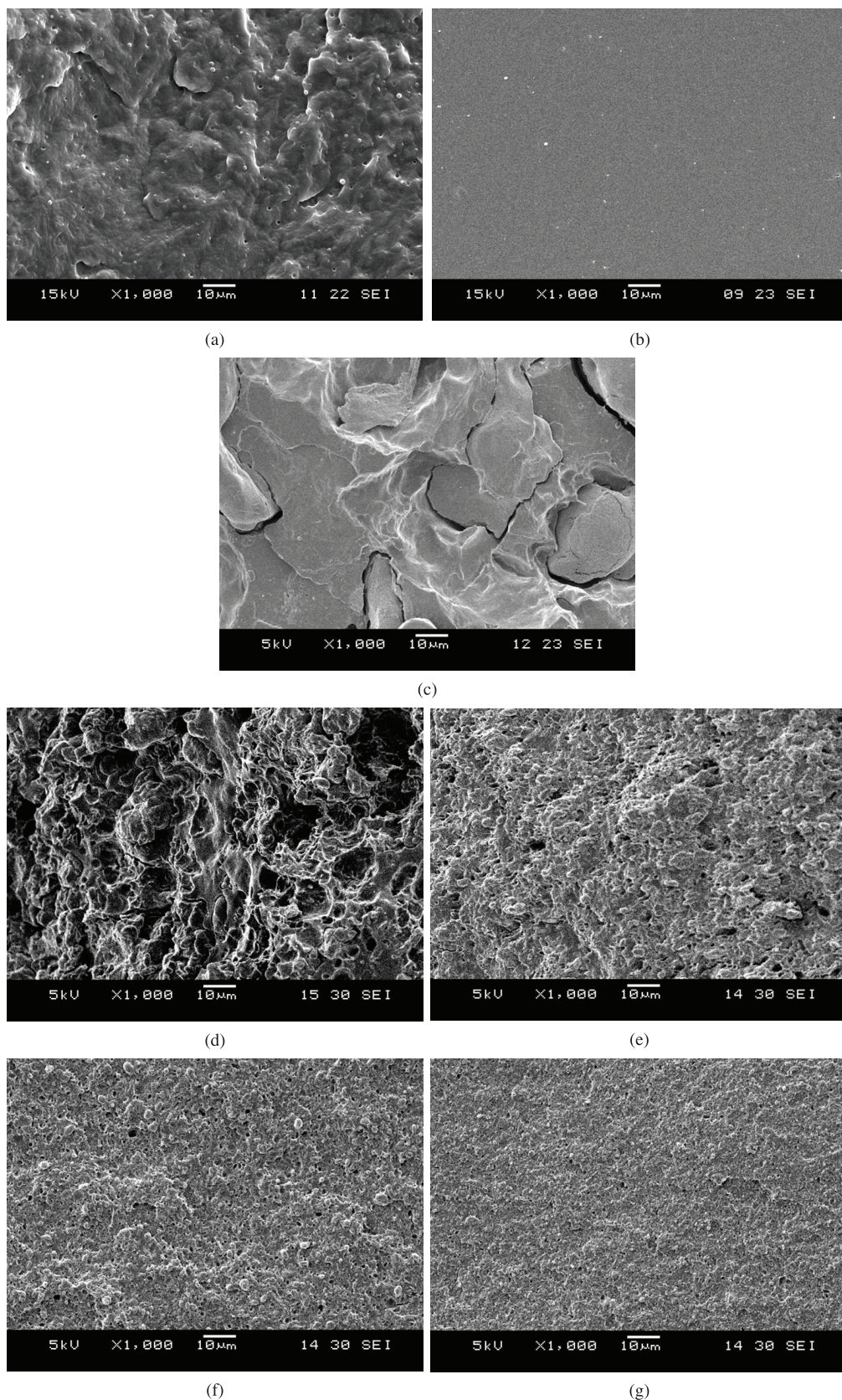
**Figure 1.** SEM images for fractured surfaces of PHBV (a), TPS (b), PHBV/TPS 1:1 neat blend (c), PHBV/TPS 1:1 blends with the addition of 2.5 (d), 5.0 (e), 7.5 (f) and 10 (g) wt% C30B.

The crystallinity of PHBV, TPS, and their 1:1 blends was investigated within the 2-35º (2θ) region (Figure 2a). Similarly to the data reported by other authors[43], high-intensity reflections at 13º and 17º (2θ) were visualized in the diffractogram for the crystalline PHBV (trace II). For TPS (trace I), the presence of $V_H$-type crystals, related to processing-induced aggregation of amylose single helices, was evidenced by the reflection at ~20º (2θ). For the blends, although the same PHBV reflections were observed, their intensity was reduced. Also, the TPS V-type reflection was shifted to a higher 2θ value and indicated the presence of $V_A$-type starch crystals, which may be related to the less hydrophilic environment surrounding these crystals in the blends. It is important to notice that the decrease in the crystalline fractions of PHBV and starch in the blends paralleled the amount of added C30B. Particularly for the blend prepared with
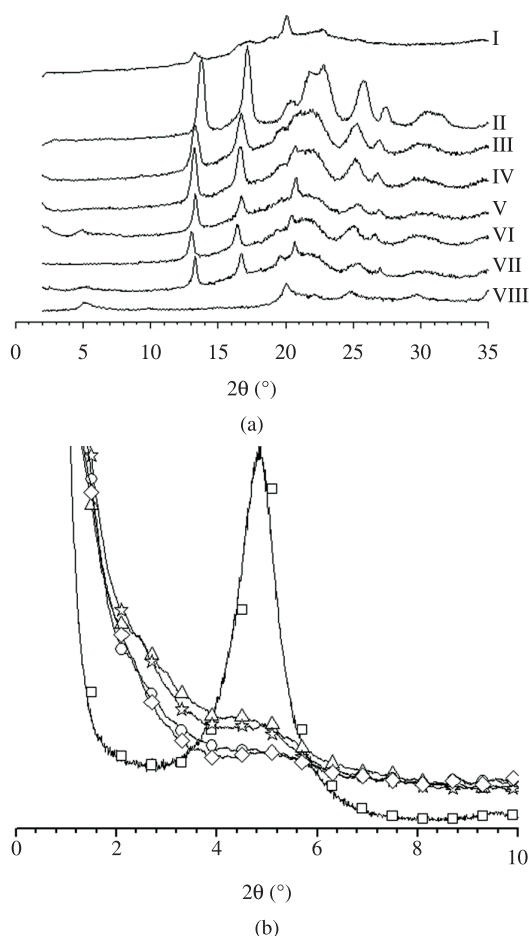
the addition of 10 wt% organoclay, the reduction in crystallinity was quite significant.

In Figure 2b, using a diffractometer with a higher resolution at a lower 2θ angular region, it was possible to investigate the degree of dispersion of C30B within the blends. The 001 reflection for the neat C30B at 2θ = 4.6º ($d_{001}$ = 1.9 nm) was also observed in the hybrids diffractograms, and indicated the presence of the organoclay tactoids. The low intensity of these reflections, associated with the absence of other reflections at a lower 2θ angular region suggested a good dispersion of C30B.

One of the main drawbacks to using starch-based materials consists of their high hydrophilicity. Water is a plasticizer for starch; water absorption leads to increasing mobility and, consequently, to the reduction of their glass transition temperatures. With increased mobility, starch molecules tend to reorganize and aggregate themselves. Accordingly, any improvement in water resistance is important. Incorporation of the less hydrophilic PHBV and C30B into the starch matrix was able to reduce the humidity absorption of the extruded materials as shown in Figure 3. While TPS reached a pseudo plateau around 80 h after the beginning of the experiment, the maximum water absorption of PHBV was 0.45% of its dry weight. The maximum humidity absorption of the 1:1 PHBV/TPS neat blend was 6.3%, whereas decreasing values of humidity absorption were observed as the C30B content was increased. This result corroborates the XRD results and is in agreement with the property of organoclays as a barrier against humidity. Moreover, humidity absorption results seemed to indicate the presence of C30B not only at the interface, but also as dispersed particles within the starch matrix.

The mechanical properties of TPS and PHBV differ significantly. PHBV is a brittle thermoplastic at room temperature, with Young's modulus (E), tensile strength at break ($\sigma_{max}$) and elongation at break ($\varepsilon_{max}$) values found in this work of 1271.0 ± 3.7 MPa, 35.8 ± 0.1 MPa, and 3.5 ± 0.1%, respectively. On the other hand, glycerol



**Figure 2.** (a) X-ray diffractograms for TPS (trace I), PHBV (trace II), TPS/PHBV neat blend at 70:30 composition (trace III), for TPS/PHBV blends at 1:1 composition with the incorporation of 2.5 wt% C30B (trace IV), 5 wt% C30B (trace V), 7.5 wt% C30B (trace VI), 10 wt% C30B (trace VII), and for C30B alone (trace VIII) in the 2θ region of 2º to 35º; (b) in the 2θ region of 0.6º to 10º for C30B alone (□),for TPS/PHBV blends at 1:1 composition with the incorporation of 2.5 wt% C30B (◇),5 wt% C30B (○),7.5 wt% C30B (☆) and 10 wt% C30B (△).
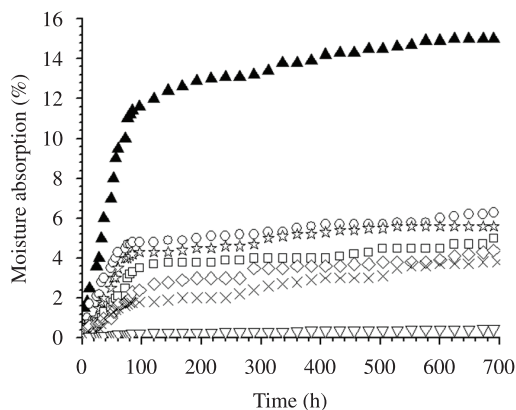


**Figure 3.** Moisture absorption for PHBV (▽), TPS (▲), neat PHBV/TPD 1:1 neat blend (○), PHBV/TPS 1:1 blends with the addition of 2.5 (☆), 5.0 (□), 7.5 (◇) and 10 (×) wt% C30B.

plasticized TPS (with glycerol at a 25 wt% content) is a soft material, and presented Young's modulus, tensile strength at break and elongation at break values of 88.0 ± 4.5 (MPa), 4.1 ± 0.2 (MPa), and 35.3 ± 2.6%, respectively. Remarkably deteriorated properties in relation to PHBV would be expected for their 1:1 blend, but some improvement would be expected with the incorporation of the organoclay, mainly in relation to TPS alone. Indeed, this was observed for the Young's modulus and the tensile strength values, as shown in Figure 4. However, owing to the stiffening effect of the organoclay, the elongation at break slightly decreased



as the organoclay content increased. It is interesting to notice that the elongation at break value was reduced even for the 1:1 neat blend, in relation to PHBV alone, reflecting the rigid nature of this polymer.

As for the materials degradation, two processes can be involved according to the environment and the material nature; simple hydrolysis (nonenzymatic) or/and enzymatic action of extracellular depolymerases (biodegradation)[44]. In the present work, the degradation of PHBV, TPS, PHBV/TPS 1:1 neat blend and the hybrids was investigated by soil burial tests. Figure 5 shows the evolution of the materials remaining weight as a function of incubation time. An increase in weight was observed during the first two weeks, attributed to water absorption because it varied with the hydrophilic nature of the sample. After 150 days, TPS was completed biodegraded.

Similarly to reported results[45,46], the degradation of PHBV occurred from the surface. As the degradation proceeded, the films became thinner, but maintained their integrity up to the end of the 150 days of tests. SEM micrographs obtained for PHBV after incubation for 150 days (75% degradation) showed the fractured surface practically intact (Figure 6a), whereas the external surface was very eroded (Figure 6b). Contrarily, for TPS films, the presence of microorganisms was observed on both surfaces (Figure 6c, d). For the PHBV/TPS/C30B hybrid materials, the films became thinner and physical integrity was visualized for only 60 days. After longer incubation times, erosion was also observed at the borders. The hybrid materials degraded faster than PHBV. The starch composition, their higher surface roughness and lower crystallinity influenced this result. After incubation for 150 days, the higher the amount of incorporated organoclay, the faster was the biodegradation in soil, reaching 76 to 90% as the C30B content was increased from 2.5 to 10 wt%. Similar SEM images as those shown for TPS biodegraded specimens were observed for the hybrids after 150 days of incubation, in which the presence of cavities and of a consortium of microorganisms was imaged.
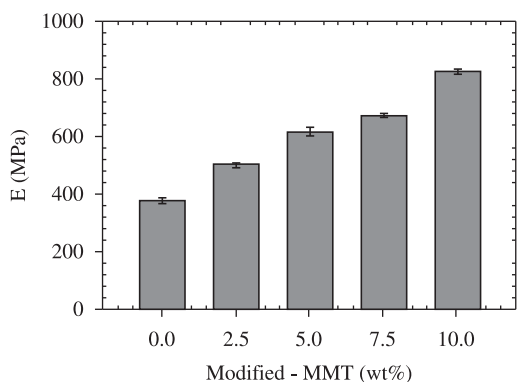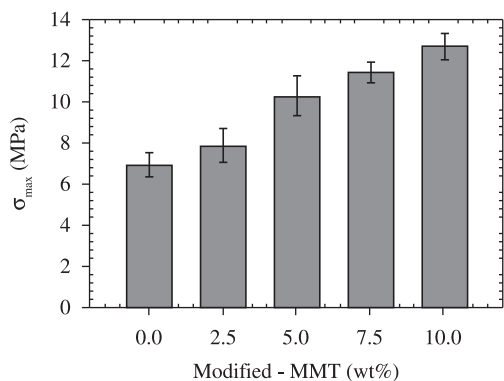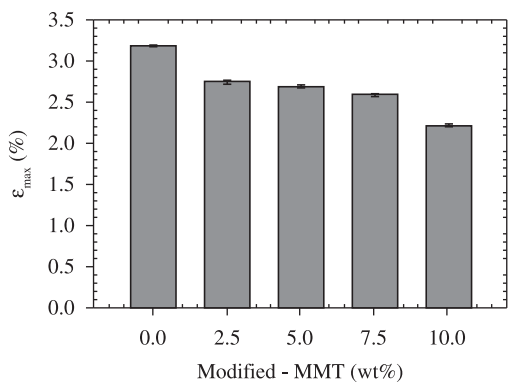
**Figure 4.** Tensile properties for PHBV/TPS/C30B materials; Young's modulus (a), tensile strength at break (b) and elongation at break (c).
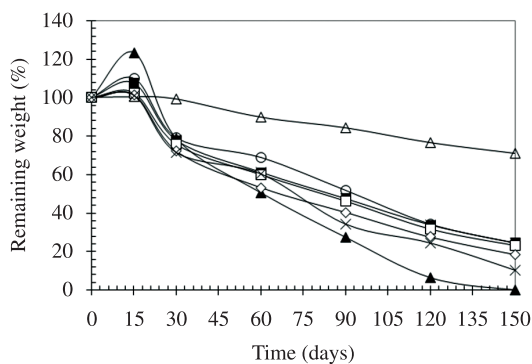


**Figure 5.** Weight loss as a function of incubation time for PHBV ($\Delta$), TPS ($\blacktriangle$), PHBV/TPS neat blend ($\circ$), and for PHBV/TPS/C30B materials with the addition of 2.5 ($\blacksquare$), 5.0 ($\square$), 7.5 ($\diamond$) and 10.0 ($\times$) wt% of C30B.
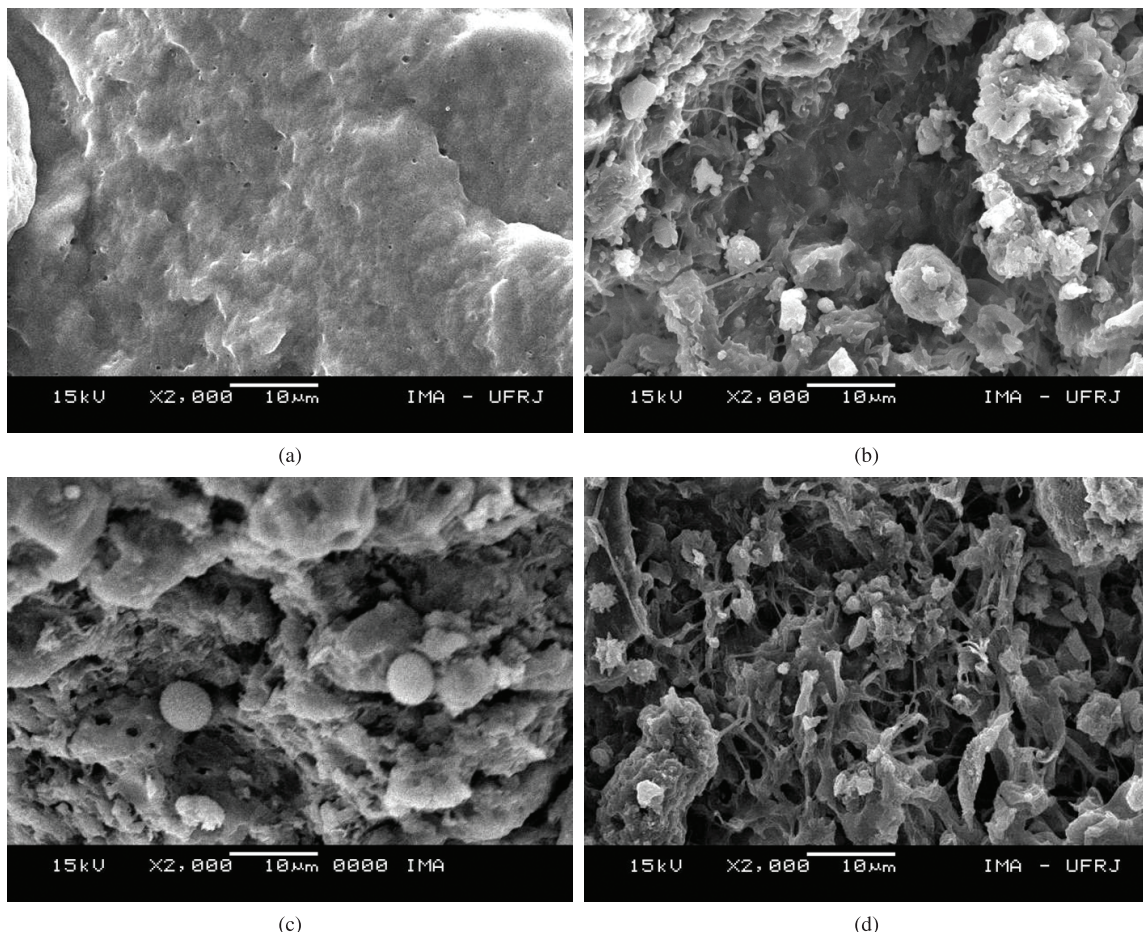
(a)

(b)

(c)

(d)

**Figure 6.** SEM images for the biodegraded PHBV and TPS; PHBV fractured surface (a) and surface (b), TPS fractured surface (c) and surface (d).

## Conclusions

Using a co-rotating twin-screw extruder, the extrusion of PHBV and its blends was successfully achieved at temperatures lower than the PHBV melting point. Under the conditions used, the starch granular structure was disrupted completely. Addition of increasing contents of the modified montmorillonite led to the improvement of the interfacial adhesion between the continuous starch phase and the PHBV dispersed phase, and to a finer morphology for the 1:1 blends. This result strongly suggested the role of the modified organoclay as a compatibilizing agent for the immiscible polymer pair, and their presence at the interface. XRD data obtained for the hybrids revealed the reduction in crystallinity and a high degree of dispersion and exfoliation of the organoclay particles. The location of clay particles also within the TPS continuous phase was suggested by the improving resistance to humidity absorption found for the nanocomposites. The reinforcing effect of the clay platelets and also of the PHBV more rigid dispersed phase contributed to the improved mechanical properties of the blend nanocomposites in relation to TPS alone. Moreover, results from soil burial tests revealed the faster biodegradation of the blend nanocomposites in relation to PHBV.

## Acknowledgements

## References

1. Álvarez-Chávez, C. R.; Edwards, S.; Moure-Eraso, R. & Geiser, K. – J. Cleaner Production, **23**, p.47 (2012). http://dx.doi.org/10.1016/j.jclepro.2011.10.003

2. Gahleitner, M. & Doshev, P. – "*Technical performance of biodegradable polymers as compared to polyolefins*", *in:* BiPoCo2012-eAbstract Book, Siófok – Hungary, May (2012).

3. Owen, A. J.; Heinzel, J.; Škrbić, Ž. & Divjakovi, V. – Polymer, **33**, p.1563 (1992). http://dx.doi.org/10.1016/0032-3861(92)90139-N

4. Ha, C.-S. & Cho, W.-J. – Progr. Polym Sci., **27**, p.759 (2002). http://dx.doi.org/10.1016/S0079-6700(01)00050-8

5. Xie, Y.; Kohls, D.; Noda, I.; Schaefer, D. W. & Akpalu, Y. A. – Polymer, **50**, p.4656 (2009). http://dx.doi.org/10.1016/j.polymer.2009.07.023

6. Noda, I.; Green, P. R.; Satkowski, M. M. & Schechtman, L. A. – Biomacromolecules, **6**, p.580 (2005). PMid:15762616. http://dx.doi.org/10.1021/bm049472m

7. Wang, S.; Song, C.; Chen, G.; Guo, T.; Liu, J.; Zhang, B. & Takeuchi, S. – Polym. Degrad. Stab., **87**, p.69 (2005). http://dx.doi.org/10.1016/j.polymdegradstab.2004.07.008

8. Maiti, P.; Batt, C. A. & Giannelis, E. P. – Biomacromolecules, **8**, p.3393 (2007). PMid:17958439. http://dx.doi.org/10.1021/bm700500t

9. Singh, S.; Mohanty, A. K., Sugie, T.; Takai, Y. & Hamada, H. - Compos.: Part A, **39**, p.875 (2008). http://dx.doi.org/10.1016/j.compositesa.2008.01.004

10. Ten, E.; Turtle, J.; Bahr, D.; Jiang, L. & Wolcott, M. - Polymer, **51**, p.2652 (2010). http://dx.doi.org/10.1016/j.polymer.2010.04.007

11. Botana, A.; Mollo, M.; Eisenberg, P. & Sanchez, R. M. T. – Appl. Clay Sci., 47, p.263 (2010). http://dx.doi.org/10.1016/j.clay.2009.11.001

12. Zhijiang, C.; Chengwei, H. & Guang, Y. – Carbohydr. Polym., **87**, p.650 (2012).

13. Corrêa, M. C. S.; Branciforti, M. C.; Pollet, E.; Agnelli, J. A. M.; Nascente, P. A. P. & Avérous, L. – J. Polym. Environ., **20**, p. 283 (2012). http://dx.doi.org/10.1007/s10924-011-0379-0

14. Imam, S. H.; Chen, L.; Gordon, S. H.; Shogren, R. L.; Weisleder, D. & Greene, R. V. – J. Environ. Polym. Degrad., **6**, p.91 (1998). http://dx.doi.org/10.1023/A:1022806222158

15. Avella, M. & Errico, M. E. – J. Appl. Polym Sci., **77**, p.232 (2000). http://dx.doi.org/10.1002/(SICI)1097-4628(20000705)77:1<232::AID-APP30>3.0.CO;2-Z

16. Chun, Y. S. & Kim, W. N. – Polymer, **41**, p.2305 (2000). http://dx.doi.org/10.1016/S0032-3861(99)00534-0

17. Chang-Sik Ha, C.-S. & Cho, W.-J. - Prog. Polym. Sci., **27**, p.759 (2002).

18. Godbole, S.; Gote, S.; Latkar, M. L. & Chakrabarti, T. – Bioresource Technol., **86**, p.33 (2003). http://dx.doi.org/10.1016/S0960-8524(02)00110-4

19. Qiu, Z.; Ikehara, T. & Nishi, T. – Polymer, **44**, p.7519 (2003). http://dx.doi.org/10.1016/j.polymer.2003.09.029

20. Lai, S.-M.; Don, T.-M. & Huang, Y.-C. – J. Appl. Polym. Sci., **100**, p.2371 (2006). http://dx.doi.org/10.1002/app.23085

21. Parulekar, Y. & Mohanty, A. K. – Macromol. Mater. Eng., **292**, p.1218 (2007). http://dx.doi.org/10.1002/mame.200700125

22. Belhassen, R.; Méndez, J. A.; Boufi, S.; López, J. P.; Puig, J.; Pèlach, A. & Mutjé, P. – J. Appl. Polym. Sci., **114**, p.313 (2009). http://dx.doi.org/10.1002/app.30567

23. Pachekoski, W. M.; Agnelli, J. A. M. & Belem, L. P. – Mater. Res., **12**, p.159 (2009). http://dx.doi.org/10.1590/S1516-14392009000200008

24. Pellicano, M.; Pachekoski, W. & Agnelli, J. A. M. – Polímeros, **19**, p.212 (2009). http://dx.doi.org/10.1590/S0104-14282009000300009

25. Tao, J.; Song, C.; Cao, M.; Hu, D.; Liu, L.; Liu, N. & Wang, S. – Polym. Degrad. Stab., **94**, p.575 (2009). http://dx.doi.org/10.1016/j.polymdegradstab.2009.01.017

26. Guo, L.; Sato, H.; Hashimoto, T. & Ozaki, Y. – Macromolecules, **43**, p.3897 (2010). http://dx.doi.org/10.1021/ma100307m

27. Parra, D. F.; Rosa, D. S.; Rezende, J.; Ponce, P. & Lugão, A. B. – J. Polym. Environ., **19**, p.918 (2011). http://dx.doi.org/10.1007/s10924-011-0353-x

28. Zhang, M. & Thomas, N. L. – J. Appl. Polym. Sci., **116**, p.688 (2010).

29. Nanda, M. R.; Misra, M. & Mohanty, A. K. – Macromol. Mater. Eng., **296**, p.719 (2011). http://dx.doi.org/10.1002/mame.201000417

30. Ma, P.; Hristova-Bogaerds, D. G.; Lemstra, P. J.; Zhang, Y. & Wang, S. - Macromol. Mater. Eng., **297**, p.402 (2012). http://dx.doi.org/10.1002/mame.201100224

31. Martelli, S. M.; Sabirova, J.; Fakhoury, F. M.; Alicja Dyzma, A.; Meyer, B. & Soetaert, W. - LWT - Food Sci. Technol., **47**, p.386 (2012).

32. Suttiwijitpukdee, N.; Sato, H.; Unger, M. & Ozaki, Y. – Macromolecules, **45**, p.2738 (2012). http://dx.doi.org/10.1021/ma201598s

33. Avella, M.; Errico, M. E.; Rimedio, R. & Sadocco, P. – J. Appl. Polym. Sci., **83**, p.1432 (2002). http://dx.doi.org/10.1002/app.2304

34. Khatua, B. B.; Lee, D. J.; Kim, H. Y. & Kim, J. K. - Macromolecules, **37**, p.2454 (2004). http://dx.doi.org/10.1021/ma0352072

35. Si, M.; Araki, T.; Ade, H.; Kilcoyne, A. L. D.; Fisher, R.; Sokolov, J. C. & Rafailovich, M. H. - Macromolecules, **39**, p.4793 (2006). http://dx.doi.org/10.1021/ma060125+

36. Kelarakis, A.; Giannelis, E. P. & Yoon, K. - Polymer, **48**, p.7567 (2007). http://dx.doi.org/10.1016/j.polymer.2007.11.005

37. Vo, L. T. & Giannelis, E. P. - Macromolecules, **40**, p.8271 (2007). http://dx.doi.org/10.1021/ma071508q

38. Ferreira, K. R. M.; Leite, I. F.; Siqueira, A. S.; Raposo, C. M. O.; Carvalho, L. H. & Silva, S. M. L. – Polímeros, **21**, p.421 (2011). http://dx.doi.org/10.1590/S0104-14282011005000072

39. Magalhães, N. F. & Andrade, C. T. – Carbohydr. Polym., **75**, p.712 (2009). http://dx.doi.org/10.1016/j.carbpol.2008.09.020

40. Magalhães, N. F. & Andrade, C. T. – J. Braz. Chem. Soc., **21**, p.202 (2010). http://dx.doi.org/10.1590/S0103-50532010000200003

41. Aouada, F. A.; Mattoso, L. H. C. & Longo, E. – Ind. Crop. Prod., **34**, p.1502 (2011). http://dx.doi.org/10.1016/j.indcrop.2011.05.003

42. Fenouillot, F.; Cassagnau, P. & Majesté, J.-C. – Polymer, **50**, p.1333 (2009). http://dx.doi.org/10.1016/j.polymer.2008.12.029

43. Bloembergen, S.; Holden, D. A.; Hamer, G. K.; Bluhm, T. L. & Marchessault, R. H. - Macromolecules, **19**, p.2865 (1986). http://dx.doi.org/10.1021/ma00165a034

44. Mallardé, D.; Valière, M.; David, C.; Menet, M. & Guérin, P. – Polymer, **39**, p.3387 (1998). http://dx.doi.org/10.1016/S0032-3861(97)10172-0

45. Phukon, P.; Saikia, J. P. & Konwar, B. K. – Colloids Surf., B, **92**, p.30 (2012). PMid:22154099. http://dx.doi.org/10.1016/j.colsurfb.2011.11.011