Characterization of Minerals, Metals, and Materials 2016
Edited by: Shadia Jamil Ikhmayies, Bowen Li, John S. Carpenter, Jiann-Yang Hwang, Sergio Neves Monteiro, Jian Li, Donato Firrao, Mingming Zhang, Zhiwei Peng, Juan P. Escobedo-Diaz, and Chenguang Bai
TMS (The Minerals, Metals & Materials Society), 2016

EFFECTS OF CARBON BLACK INCORPORATION ON MORPHOLOGICAL, MECHANICAL AND THERMAL PROPERTIES OF BIODEGRADABLE FILMS

Julio Harada[1,2]; José Ricardo N. Macedo[1]; Glauson Aparecido F. Machado[2]; Francisco Valenzuela-Díaz[3]; Esperidiana A. B. Moura[2]; Derval S. Rosa[1]

[1]Universidade Federal do ABC – UFABC, Av. dos Estados, 5001, São Paulo, SP, 09210-580, Brasil
[2]Instituto de Pesquisas Energéticas e Nucleares – IPEN-CNEN/SP
Av. Prof. L. Prestes, 2242 São Paulo, SP, 05508-000, Brasil
[3]Universidade de São Paulo, Escola Politécnica, Dep. de Eng. Metalúrgica e de Materiais. Av. Prof. Mello de Moraes, 2463, São Paulo, SP, 05508-030 – Brasil

Keywords: Biodegradable Films, Carbon Black, Mechanical Properties, FE-SEM

Abstract

This work evaluates the effects of carbon black incorporation on morphological, mechanical and thermal properties of biodegradable films. The biodegradable composite films based on PBAT/PLA blend and PBAT/PLA blend containing 2 wt. % of carbon black were prepared by melt extrusion, using a twin screw extruder machine and blown extrusion process. The properties of biodegradable film samples were investigated by tensile tests, XRD, MFI, TGA, DSC and FE-SEM analysis and the correlation between properties was discussed.

Introduction

Increasing interest in new materials based on blends of two or more polymers has been observed during the last decades. Conventional thermoplastic polymers have good mechanical properties and thermal stability, much better than the biodegradable ones. Biopolymers have advantages over the conventional polymers; biopolymers are from renewable materials and can be biodegradable. There is also a limitation in the performance and application of biopolymers in comparison to conventional thermoplastics. Therefore, the extensive application of these biopolymers is still challenged by one or more of their possible inherent limitations, such as poor processability, brittleness, hydrophilicity, poor moisture and gas barrier, inferior compatibility, poor electrical, thermal and mechanical properties [1, 2]. Blends of conventional plastics (petroleum-derived polymers) and biopolymer can form a new class of materials with improved mechanical properties compared with those of single components. Polymer blending offers possibility of adjusting the cost-performance balance and tailoring the technology to make products for specific end-use applications; extends engineering resins' performance; improves specific properties or solvent resistance; and provides means for industrial and consumer plastics waste recycling [3].

Combination of polymer blends with micro or nanofillers appears quite promising based on balanced performance of biopolymer, to compare better thermal and mechanical properties, improve service temperature, moisture resistance, gas barrier, and in some cases reduce the cost of biodegradable thermoplastic polymers. Incorporation of nanoparticles into polymer materials has attracted a great deal of attention due to its ability to enhance polymer properties such as thermal, mechanical, and gas barrier [1]. Inorganic materials due to their ability in harsh process conditions, such as metal or metal oxides have attracted a great deal of attraction recently. Carbon Black among the inorganic materials have particular interesting due to both safe material for animals and human and stability under harsh condition processes [4, 5].

The synthesis of inorganic-biopolymer nanocomposites has been intensely studied due to their unique combination of properties and widespread potential applications. These generations of biocomposites have more desirable functional properties, such as good mechanical strength, and low water vapor permeability. Lately, researchers have reported the improvements of biopolymer properties by incorporation of nanoparticles, such as clay, silica, layered silicate nanoparticles, calcium carbonate, zinc oxide and titanium dioxide. In general, these researchers have reported that the incorporation of nanoparticles improve mechanical properties, as well as barrier and antimicrobial properties of biopolymers [6,7].

The aim of this study was to process and investigate the changes in the mechanical, morphological and environmental UV protection of the biodegradable PBAT/PLA blend due to the incorporation of Carbon Black nanoparticle.

Materials and Methods

Materials:

The materials used in this work were biodegradable aliphatic-aromatic copolyester (PBAT); biodegradable poly(lactic acid) (PLA), and Carbon Black nanoparticles.

Preparation of blend and composite:

PLA, PBAT, and the Carbon Black nanoparticle were dried at 60 ± 2 ºC for 4 h to reduce its moisture content to less than 2 %. The PBAT/PLA blend (59 %/ 39 %, based on wt. %) with 2 wt. % of Carbon Black addition were prepared by melting extrusion process, using a co-rotating twin-screw, with 20 mm of diameter, Haake Rheomex P 332 extruder. The temperature profile was 135/145/148/150/150/150 ºC. Screw speed was 180 rpm. The extrudates coming out of the extruder were cooled down in air for a better dimensional stability, pelletized by a pelletizer, dried again at 60 ± 2 ºC for 4 h and fed into extrusion blown film, single screw machine with 25 mm diameter, Carnevalli, and specimens test samples were obtained.

Characterization

Mechanical tests:

Tensile tests: tensile tests were performed using an INSTRON 5900 with 500 kg load cell and 50mm.min^{-1}, according to ASTM D 638, in order to evaluate the mechanical behavior of the materials studied.

X-rays diffraction (XRD) tests:

X-rays diffraction (XRD) were recorded on a BRUKER, Focus-D8 diffractometer operated at 40 kV and 40 mA, with CuKα radiation (λ= 1.54 Å).

Melt Flow Index (MFI) measurements:

Melt Flow Rate (ASTM D1238) were carried out using CEAST Melt Flow modular line at 190°C / 2.16 kg. MFI measurements were determined work in order to evaluate the Carbon Black addition on blow film extrusion process.

Thermogravimetric analysis (TG):

Thermogravimetric analysis was performed using an appliance STA 449 F3 Jupiter of Netzch with analysis from 25 to 500°C under a rate of 10°C.min^{-1} in an atmosphere of N_2.

Differential scanning calorimetry analysis (DSC):

DSC analyses were carried out using a Mettler Toledo DSC 822 from 25 to 250°C at a heating rate of 10 °C/min under oxygen atmosphere.

Field Emission Scanning Electron Microscopy (FE-SEM):

FE-SEM were carried out using a JEOL-JSM-6701 F, microscope with an accelerating voltage of 1-30 kV, using EDS Thermo-Scientific mod. Noran System Six software, in carbon sputtered samples.

Results and Discussion

Mechanical tests results:

Tensile test results: The Table I presents the results of tensile tests of PBAT/PLA blend and PBAT/PLA/Carbon Black nanocomposite. These results shown the average values calculated from the data obtained in tests for five test specimens. As can be seen in this table, the addition of Carbon Black in PBAT/PLA blend improved the tensile strength at break (of around 100 %), elongation at break and modulus properties of blend. The improve of tensile properties in PLA due to Carbon Black has been reported in the literature by Chivrac, et al. [8] and Luduena, et al. [9]. These authors suggested that Carbon Black could be acting as nucleating agent improving the crystallinity of PLA.

Table I. Tensile test results of PBAT/PLAblend and PBAT/PLA/Carbon Blacknanocomposite.

Sample	Young's modulus (MPa)	Tensile strength at break (MPa)	Elongation at break (%)
PBAT/PLA Blend	41 ± 19	6 ± 3	326 ± 94
PBAT/PLA+2%CB	78 ± 9	12 ± 1	430 ± 27

Figure 1 shows the diagram stress against strain for PBAT/PLA blend and PBAT/PLA/Carbon Black nanocomposite. From this Figure it is possible to observe that the behavior of nanocomposites perfectly elastic, the stress increases linearly with strain. However, Carbon Black addition caused a significant increase on tensile strength and elongation of blend.

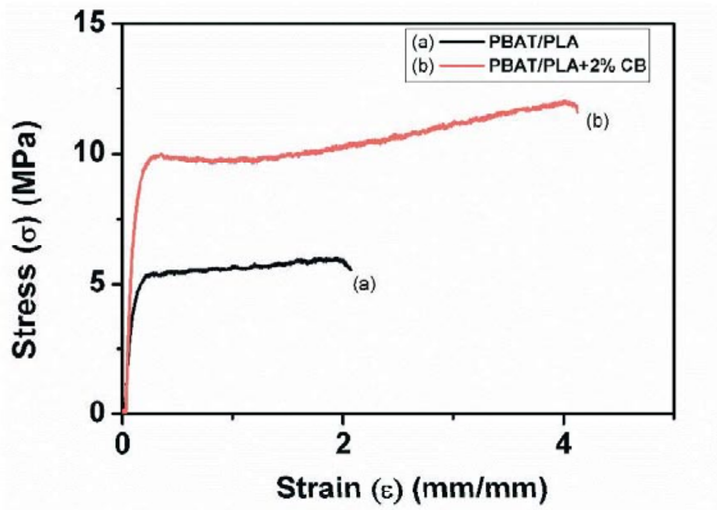

Figure 1. Diagram stress (MPa) against strain (mm/mm) for PBAT/PLA blend and PBAT/PLA/Carbon Black nanocomposite.

X-ray diffraction (XRD) analysis results:

The XRD patterns of PBAT/PLA blend and PBAT/PLA/Carbon Black nanocomposite are shown in Figure 2.

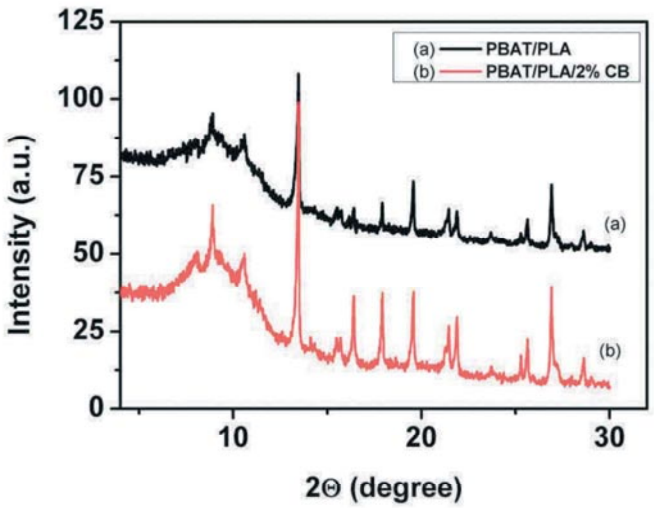

Figure 2. XRD diffraction patterns for the PBAT/PLA blend and PBAT/PLA/Carbon Black nanocomposite in the range of 2θ between 4° to 30°.

It can be seen in Figure 2, the XRD pattern of PBAT/PLA blend showed a prominent 2θ peak at around 16.4º, which has increased intensity due to Carbon Black nanoparticle addition. From this figure, it can be observed that two new 2θ peaks at around 8.1º and 8.9º that may be related to the Carbon Black structure.

Melt flow index (MFI) measurements:

The MFI values of PBAT/PLA blend and PBAT/PLA/Carbon Black nanocomposite are presented in Table II. The MFI value of PBAT/PLA presented reduction due to Carbon Black addition. These results suggest that Carbon Black incorporation may have caused a reduction of the mobility of the PBAT/PLA blend chains.

Table II. MFI results for the PBAT/PLA blend and PBAT/PLA/Carbon Black nanocomposite.

Sample	MFI ($g.10min^{-1}$)
PBAT/PLA Blend	27 ± 3
PBAT/PLA+2%CB	23 ± 3

Thermogravimetric analysis (TG) results:

Figure 3 shows the TG thermograms of PBAT/PLA blend and PBAT/PLA/Carbon Black nanocomposite. The decomposition temperature and weight loss of PBAT/PLA/Carbon Black nanocomposite are presented in Table III. It can be seen in Figure 3 and Table III that Carbon Black nanoparticle addition reduced the degradation temperature of PBAT/PLA blend.

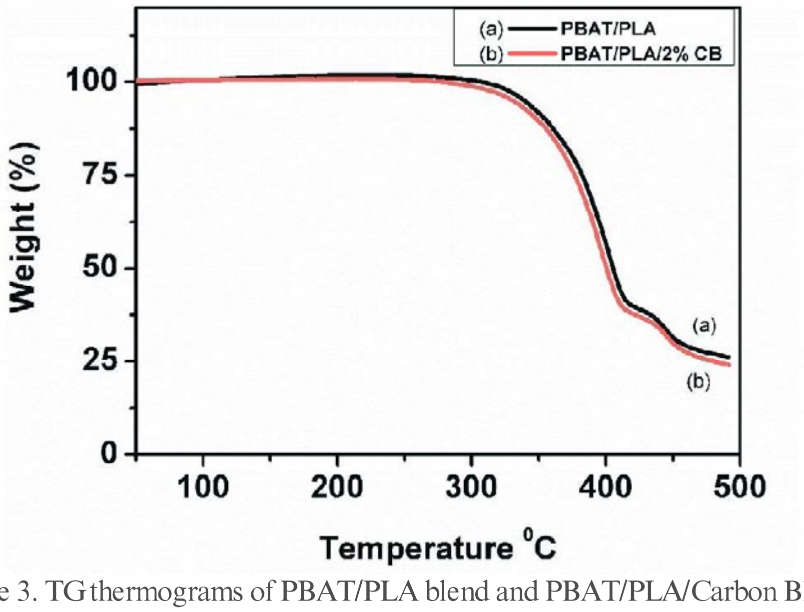

Figure 3. TG thermograms of PBAT/PLA blend and PBAT/PLA/Carbon Black nanocomposite.

Table III. Decomposition temperature and weight loss of PBAT/PLA blend and PBAT/PLA/Carbon Black nanocomposite.

Sample	T_{onset} (°C)	T_{max} (°C)	Weight Loss (%)
PBAT/PLA Blend	347.54	410.44	74.08
PBAT/PLA+2%CB	343.78	407.23	76.01

Differential Scanning Calorimetry (DSC) analysis results:

DSC curves for the PBAT/PLA blend and PBAT/PLA/Carbon Black nanocomposite can be seen in Figure 4. From Figure 4, it could be inferred that compared with the PBAT/PLA blend the endothermic melting enthalpy of PBAT/PLA blend increased considerably due to Carbon Black nanoparticle addition. The increases in the melting enthalpy can be attributed to the increase in crystallinity of PBAT/PLA composite.

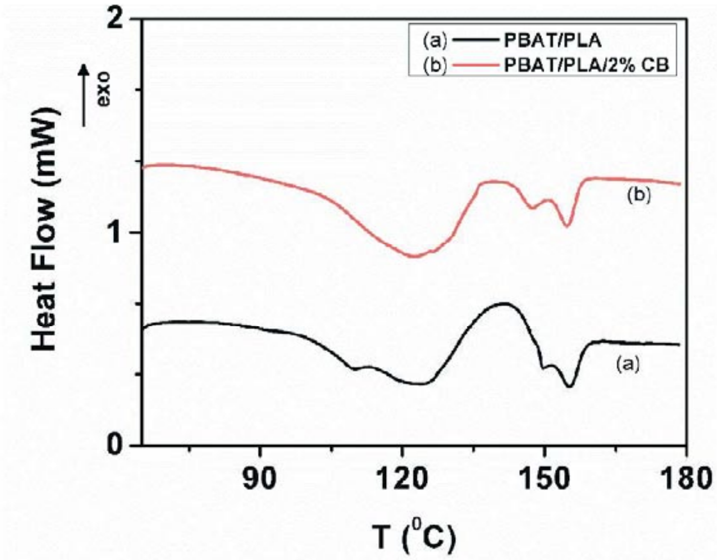

Figure 4. DSC analysis for the PBAT/PLA blend and PBAT/PLA/Carbon Black nanocomposite.

Table IV show the average values of melting temperature (Tm) and melting enthalpy (ΔHm) of the PBAT/PLA blend and PBAT/PLA/Carbon Black nanocomposite.

Table IV. The average values of Melting temperature (Tm) and melting enthalpy (ΔHm) of the PBAT/PLA blend and PBAT/PLA/Carbon Black nanocomposite.

Sample	Tm^1 (°C)	Tm^2 (°C)	ΔHm ($J.g^{-1}$)
PBAT/PLA Blend	124	155	4.4
PBAT/PLA+2%CB	123	154	7.2

From Figure 4 and Table IV, it can be observed two melting temperatures (Tm^1 and Tm^2), which are near of the melting temperatures of PBAT and PLA respectively [10, 11]. It means that blend processing and Carbon Black nanoparticle addition had a capability to reorient the polymeric molecules present in crystal form in order to obtain a composite material with high melting enthalpy and, consequently, high crystallinity percentage.

Field Emission Scanning Electron Microscopy (FE-SEM) analysis results:

FE-SEM micrographs of PBAT/PLA blend and PBAT/PLA/Carbon Black nanocomposite in different magnifications are showed in Figure 5. As can be seen in Figure 5a, the PBAT/PLA blend with 6.000 X of magnification appeared to have a clear, phase-separated morphology with PLA dispersed in the PBAT matrix. Figure 5b and 5c shows micrographs of PBAT/PLA/Carbon Black with 6.000 X and 10.000 X of magnifications, respectively. It can be seen that there are several Carbon Black nanoparticle agglomerates in the surface of the blend. This result suggests that part of nanoparticles were not dispersed in the PBAT/PLA blend.

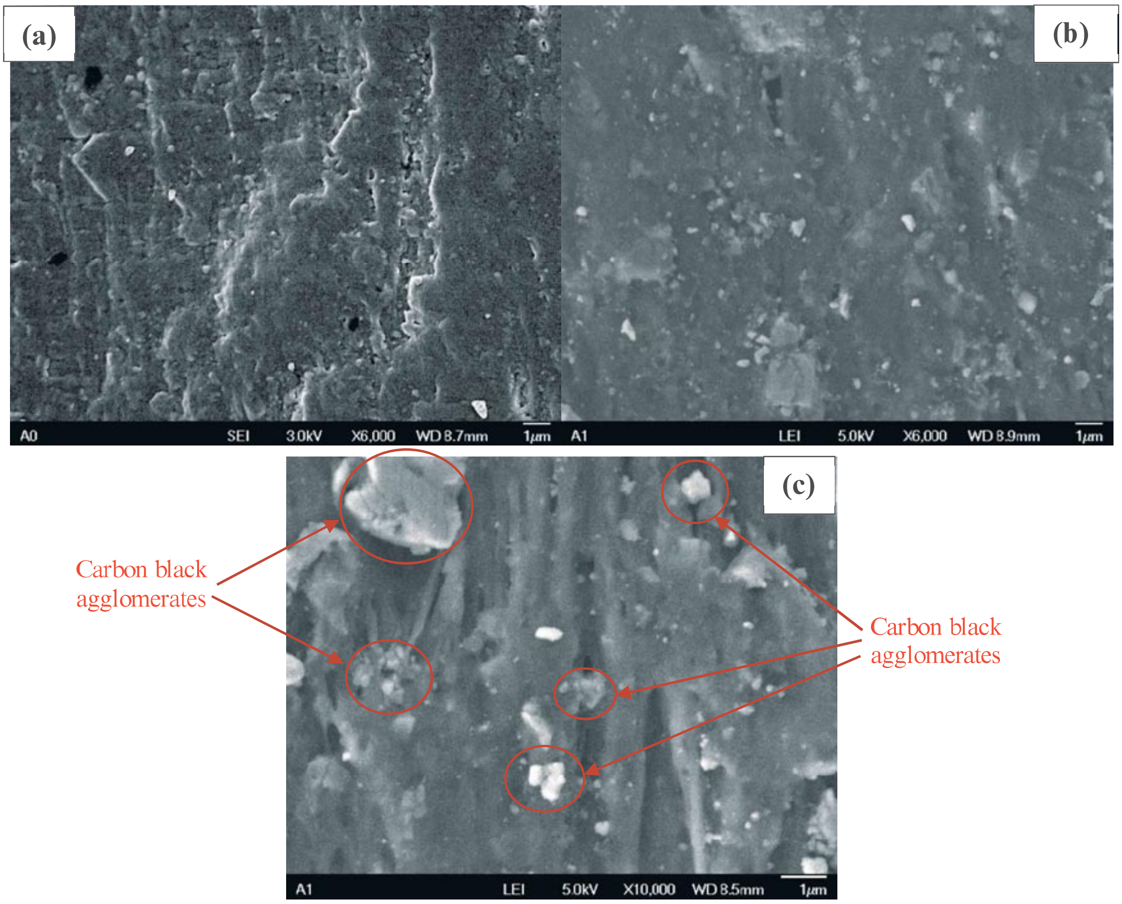

Figure 5. FE-SEM micrographs of PBAT/PLA blend and PBAT/PLA/Carbon Black nanocomposite: (a) PBAT/PLA Blend (6.000 X); (b) PBAT/PLA/Carbon Black (6.000 X); (c) PBAT/PLA/Carbon Black (10.000 X).

Conclusions

Results showed that incorporation of (2 wt. %) of Carbon Black nanoparticle in the PBAT/PLA blend matrix led to significant gain of mechanical properties of the blend. The DSC analysis results indicated that blending PBAT with PLA, followed by of Carbon Black nanoparticle addition increased considerably the melting enthalpy of PBAT/PLA blend, and consequently, increased the crystallinity percentage. Although gains in mechanical properties of the blend due to the Carbon Black addition were observed, the FE-SEM micrographs results showed that there were several Carbon Black nanoparticle agglomerates in the surface of the blend. These results indicates that Carbon Black nanoparticle addition in the PBAT/PLA matrix, despite the presence of agglomerates, improved the biodegradable blend and led to the obtaining of composite materials with superior properties suitable for several industrial application

Acknowledgements

The authors wish to thank IPEN, UFABC and MAMAPLAST for the support for this work.

References

1. R. Nassiri, A. MohammadiNafchi, "Antimicrobial and Barrier Properties of Bovine Gelatin Films Reinforced by Nano TiO_2," *Journal of Chemical Health Risks*, 3 (3) (2013), 12-28.
2. M. Kurian et al., "A Novel Route to Inducing Disorder in Model Polymer-Layered Silicate Nanocomposites," *Macromolecules*, 39 (2006), 1864-1871.
3. L.A. Utracki (ed.), Polymer Blends Handbook, vol. 1 (Kluwer Academic Publishers, Dordrecht, Chapter 1, 2003).
4. P. K. Stoimenov et al., "Metal Oxide Nanoparticles as Bactericidal Agents," *Langmuir*, 18 (2002), 6679-6686.
5. W. Lin, et al., "Toxicity of nano and micro-sized ZnO particles in human lung epithelial cells. *Journal of Nanoparticle Research*, 11 (2009), 25-39.
6. C. Chawengkijwanich, Y. Hayata, "Development of TiO2 powder-coated food packaging film and its ability to inactivate Escherichia coli in vitro and in actual tests," *International Journal of Food Microbiology*, 123 (2008), 288-292.
7. C. Bastioli (ed.), Handbook of Biodegradable Polymers (Rapra Technology, 2005).
8. F. Chivrac et al., "Aromatic Copolyester-based Nano-biocomposites: Elaboration, Structural Characterization and Properties," *J. Polym. Environ*. 14 (2006), 393-401.
9. L.N. Luduena, et al., "Extraction of Cellulose Nanowhiskers from Natural Fibers and Agricultural Byproducts," *Fibers and Polymers*, 14 (7) (2013), 1118-1127.
10. F.P. Carrasco et al., "Processing of poly(lactic acid):Characterization of chemical structure, thermal stability and mechanical properties," *Polymer Degradation and Stability*, 95 (2) (2010), 116-125.
11. P. Georgiopoulos, E. Kontou, and M. Niaounakis, "Thermomechanical Properties and Rheological Behavior of Biodegradable Composites," *Polymer Composites*, 35 (6) (2014), 1140-1149.