

Toughening of bio-PE upon addition of PCL and PEGAA

<http://dx.doi.org/10.1590/0370-44672018720027>

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Abstract

Researches of polymer blends based on biological and biodegradable polymers appear as a viable alternative to develop environmentally friendly materials. Therefore, the aim of this research was to produce compounds made with biological polyethylene, i.e., Biopolyethylene, Bio-PE, added to the biodegradable Polycaprolactone (PCL) and functionalized by the copolymer of polyethylene grafted with acrylic acid (PEgAA), to obtain better mechanical properties and toughen Bio-PE. Compounds were processed in a co-rotating twin screw extruder and sample tests were injection molded. The compositions investigated were: Bio-PE/PCL at 90/10, 80/20 and 70/30 wt.% without compatibilizer and upon addition of 10 phr (parts per hundred of resin) of PEGAA. The blends were characterized by X-ray diffraction (XRD), impact strength, heat deflection temperature (HDT) and scanning electron microscopy (SEM). Through XRD, it was observed that addition of PCL and PEGAA did not significantly change Bio-PE diffraction patterns. Impact strength data showed that the blends presented a tougher behavior upon addition of PCL and PEGAA. The HDT of compatibilized blend with 20wt.% of PCL was slightly higher. SEM images of compatibilized blends showed lower average particle diameters as well as absence of coalescence and aggregates.

Keywords: biopolymer Bio-PE, biodegradable polymer PCL, polymer blends Bio-PE/PCL/PEGAA, tough behavior.

1. Introduction

Given the main property of the vast majority of polymers - durability - a serious problem follows the contemporary man: the huge amount of garbage produced in social communities, especially in large urban centers. This garbage, consisting largely of industrialized products made from synthetic polymers, require several years to be degraded, resulting in environmental problems that can be

disastrous for the societies (Hemais *et al.*, 2000; Rosa *et al.*, 2002).

These environmental pollution problems are generated by plastic waste and have led the scientific community to reflect on feasible alternatives to solve it. For the management of the plastic waste produced in society, the "green" polymers and the biodegradable ones appear as alternatives for its solution (Rosa *et al.*, 2002; Spierling

et al., 2018a).

The use of biopolymers produced from renewable raw materials, such as: maize, sugarcane, cellulose, chitin, and others, is considered as a possible solution to reduce environmental pollution. The use of these "green" polymers, such as biopolyethylene (Bio-PE), produced from ethanol derived from sugarcane, although not biodegradable, maintains the neutral

balance of carbon dioxide (CO₂) in nature. The CO₂ captured from the atmosphere by biomass, when released to the atmosphere by combustion, is captured again by sugarcane by the process of photosynthesis in the next harvest (Brito *et al.*, 2012; Braskem, 2015; Mores *et al.*, 2018).

Another alternative for this scenario would be the use of environmentally biodegradable polymers (BDPs), which have the advantage of being stable over their useful life and being degraded in a short time after disposal in the environment.

2. Materials and methods

Materials

- High Density Polyethylene (Bio-PE), I'm green® SHC7260, Braskem. Polymer produced from sugarcane. Minimum carbon content from renewable source of 94%. Density of 0.959 g/cm³, melt flow in-

Polycaprolactone (PCL) is one of the BDPs that has arisen interest in the substitution of conventional polymers, since it has good properties and also compatibility with other materials (Swift, 1998; Braunegg *et al.*, 1998; Zuchowska, 1999).

The study of polymer blends involving these two classes of polymers appears as a viable alternative for the process of developing ecologically correct materials (eco-friendly). Moreover, the interest in the study of polymer blends is an alternative to obtain materials with properties that

are not generally found in a single material (Utracki, 2002; Matta *et al.*, 2014; Spierling *et al.*, 2018b).

Therefore, this study aimed to develop polymer blends from environmentally friendly materials, i.e., Bio-PE and PCL with the addition of PEgAA as compatibilizer, whereby the task is to produce tough Bio-PE. The blends were characterized by X-ray diffraction (XRD), impact strength, heat deflection temperature (HDT) and scanning electron microscopy (SEM).

- dex (MFI) = 7.2 g/10 min (190°C/2.16 kg).

- Polycaprolactone (PCL), Capa® 6500, MFI = 28 g/10min (160°C/2.16kg) and elongation up to 800%, produced by Perstorp Winning Formulas.

- Polyethylene grafted with 5.5-6.5% Acrylic Acid (PEgAA) Polybond 1009 (MFI = 5g/10min) supplied by Addivant.

Compounding of polymer blends

Blend compounding was performed in a co-rotating twin screw extruder from Coperion, ZSK 18 mm, operating at

200°C in all zones, 250 rpm and feed rate of 5 kg/h, the output was ground using a knife mill. Afterwards, compounds were

oven dried for 24 hours at 40°C.

The compositions of extruded blends are shown in Table 1.

Specimens	Bio-PE (%)	PCL (%)	PEgAA (phr)
Bio-PE	100	-	-
Bio-PE/PCL	90	10	-
Bio-PE/PCL/PEgAA	90	10	10
Bio-PE/PCL	80	20	-
Bio-PE/PCL/PEgAA	80	20	10
Bio-PE/PCL	70	30	-
Bio-PE/PCL/PEgAA	70	30	10

Table 1
Compositions of Bio-PE and its blends.

Specimens of Bio-PE, Bio-PE/PCL (90/10, 80/20 and 70/30 w/w) and Bio-PE/PCL/PEgAA (90/10/10, 80/20/10 and 70/30/10 w/w/phr) for impact and HDT experiments were injection

molded according to ASTM D256 and ASTM D648 standards in an Arburg Allrounder 270C Golden Edition. Processing parameters were: temperature profile = 180°C in zone 1 and 200°C

in zone 2; temperature and mold cooling time: 20°C and 45 s; and injection pressure: 800 and 1500 kg/cm². For comparison, neat Bio-PE specimens were injected using the same procedure.

Compounds characterization

X-ray diffraction (XRD)

X-ray diffraction (XRD) experiments were executed in a Shimadzu *Impact Strength*

Impact tests carried out in a CEASt Resil-5.5 impact machine operating *Heat deflection temperature (HDT)*

HDT tests carried out in a HDT 6 VICAT P/N 6921.000 instrument according to ASTM D648. Experiments *Scanning electron microscopy (SEM)*

SEM images were acquired in a Tescan Veja 3, tension 30 kV. The fracture surfaces from impact tests were analyzed.

XRD-6000 instrument in the region of 2-30° (2θ), with K_{αCu} radiation,

ating with a 2.75J pendulum on notched specimens in Izod configuration, ac-

were conducted using as load 455kPa, heating rate 120°C/h (method A), specimens were submersed in a silicone bath

In the blends, the dispersed phase (PCL) was extracted from the matrix by immersing the samples in toluene (99.5% purity and molecular weight of

tension 40 kV, current 30 mA and scan rate 2°/min.

cording to ASTM D256. An average of ten samples was analyzed.

oil. HDT was determined at 0.25mm of specimen deflection. An average of five samples was analyzed.

92.14), for 24 h. Afterwards, surfaces were coated with a gold layer (sputtering - Shimadzu Metallizer - IC-50, using a 4mA current).

3. Results and Discussion

X ray diffraction (XRD) measurements

Figure 1 shows XRD diffractograms of Bio-PE, binary (Bio-PE/PCL) and ternary blends (Bio-PE/PCL/PEgAA).

Diffractogram of Bio-PE presents peaks around 21.6° and 23.7° evidencing a presence of a typical crystalline PE orthorhombic structure, which is attributed to the planes (110) and (200), as reported by Lahor *et al.* (2010) and Stelescu *et al.* (2013).

From the diffractograms of binary

and ternary blends, it can be verified that the addition of PCL (in contents 10, 20 and 30 wt.%) and the functionalized copolymer (PEgAA) did not modify the diffraction patterns of Bio-PE matrix. However, it was observed that for binary blends with 20 and 30% PCL, there was an increase in the intensity of (200) plane, indicating an increase in the crystallinity of these compounds (Grego *et al.*, 1987; Minick *et al.*, 1995).

For the ternary blends, intensity increase of (110) and (200) planes indicated that PEgAA contributed to an increase of the crystalline phase content. According to Campoy *et al.* (1995), upon dispersion of the components in the amorphous phase due to compatibilization, it is possible to verify an increase in the relative intensity of Bio-PE reflections in the diffractograms.

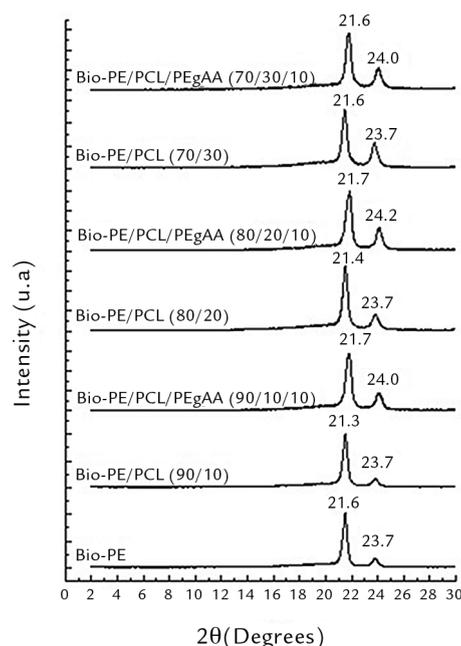


Figure 1
X ray diffratograms Bio-PE and its blends.

The crystallinity index for the samples was computed and investigated by XRD patterns. In this work, the Ruland Equation was used to evaluate this parameter (Ruland, 1964).

As presented in Table 2, the crystallinity index of Bio-PE is similar to that reported in literature (Grego *et al.*, 1987; Oliveira *et al.*, 2013).

According to the data shown in Table 2, it is observed that for the binary

blends, the crystallinity index increases upon PCL addition, which may be connected to the immiscibility between Bio-PE and PCL, where both components are crystallizable. Although these phases are physically separated, they can significantly influence the crystallization of each other (Utracki, 2002). Therefore, co-crystallization may take place, where Bio-PE and PCL form isomorphic crystals, i.e., the macromolecular chains of both polymers

share formation of the same crystallite (Hussein, 2003; Liang *et al.*, 2008).

For the ternary blends, it is verified that the crystallinity index is very similar to that of Bio-PE (Table 2). It is assumed that PEgAA changes the crystallizability of these blends, suggesting that the interaction of PEgAA with PCL occurs through crystalline and non-crystalline regions (Minick *et al.*, 1995; Utracki, 1989; Liang *et al.*, 2008).

Composition	Crystallinity Index (%)*
Bio-PE	77.3
Bio-PE/PCL (90/10 w/w)	83.2
Bio-PE/PCL/PEgAA (90/10/10 w/w/phr)	75.0
Bio-PE/PCL (80/20 w/w)	85.0
Bio-PE/PCL/PEgAA (80/20/10 w/w/phr)	79.3
Bio-PE/PCL (70/30 w/w)	89.0
Bio-PE/PCL/PEgAA (70/30/10 w/w/phr)	76.7

*Ruland Equation: $W_c = I_c / (I_c + K I_a)$, where, I_c -Integration of diffraction peaks; K- Characteristic constant of polymers, (According to Wunderlich 1980, for Polyethylene $K=1.23$). I_a -Integration of amorphous halo. I_c and I_a data were measured using the software Origin Pro 8.

Table 2
Crystallinity index of Bio-PE and its blends.

Impact Strength Measurements

The impact strength properties for Bio-PE, Bio-PE/PCL and Bio-PE/PCL/

PEgAA are shown in Table 3.

Composition	Impact strength (J/m)*
Bio-PE	34.0±1.0
Bio-PE/PCL (90/10 w/w)	36.5±3.1
Bio-PE/PCL/PEgAA (90/10/10 w/w/phr)	33.1±2.0
Bio-PE/PCL (80/20 w/w)	64.0±2.9
Bio-PE/PCL/PEgAA (80/20/10 w/w/phr)	62.4±2.4
Bio-PE/PCL (70/30 w/w)	62.3±3.8
Bio-PE/PCL/PEgAA (70/30/10 w/w/phr)	54.6±2.4

*Measurement of standard deviation was performed through spreadsheet editor in Microsoft Excel.

Table 3

Impact strength of Bio-PE and its blends.

According to data in Table 3, addition of 10% PCL did not significantly modify the impact strength of Bio-PE. Binary blends with 20 and 30% PCL exhibited a typical behavior of tough material, providing increases around 88.2% for Bio-PE/PCL (80/20 w/w) and 83.2% for Bio-PE/PCL (70/30 w/w) related to Bio-PE. Most of this trend is associated to the increase of PCL content in the mixture, since it presents elastomeric characteristics, being able to act as an impact modifier, promoting an enhancement of the system impact strength (Guimarães *et al.*, 2002; Deblieck *et al.*, 2011; Silva,

2014; Fel *et al.*, 2016; Chudnovsky and Sehanobish, 2017; Agrawal *et al.*, 2018).

Table 3 shows a similar behavior for the ternary blends compared to the binary ones. The compatibilized blends with PEgAA (80/20/10 and 70/30/10 w/w/phr) showed the highest impact strength compared to Bio-PE. This increase was approximately 83.5% for Bio-PE/PCL/PEgAA (80/20/10 w/w/phr) and 60.5% for Bio-PE/PCL/PEgAA (70/30/10 w/w/phr). This behavior can be associated to the higher adhesion among the phases increasing PCL content (20 and 30%), as a result of reaction between acrylic

acid groups and hydroxyl ones of PCL, as well as the miscibility of PEgAA with Bio-PE, which properly promotes stress transferring from one to each other phase (Deblieck *et al.*, 2011; Silva, 2014; Bezerra *et al.*, 2017a; Chudnovsky and Sehanobish, 2017; Agrawal *et al.*, 2018). Even though addition of the coupling agent did not improve the impact strength, when compared to a respective blend without functionalized copolymer, the morphology reached by SEM showed that the dispersed phase decreased and the morphology stabilized. The SEM images are presented further on in Figures 2 to 8.

Heat Deflection Temperature (HDT) Measurements

Table 4 presents HDT results for Bio-PE, Bio-PE/PCL and Bio-PE/PCL/

PEgAA compounds.

Composition	HDT (°C)*
Bio-PE	66.8±1.5
Bio-PE/PCL (90/10 w/w)	64.2±0.7
Bio-PE/PCL/PEgAA (90/10/10 w/w/phr)	65.9±0.9
Bio-PE/PCL (80/20 w/w)	60.6±1.0
Bio-PE/PCL/PEgAA (80/20/10 w/w/phr)	70.1±0.7
Bio-PE/PCL (70/30 w/w)	58.4±0.5
Bio-PE/PCL/PEgAA (70/30/10 w/w/phr)	59.8±0.7

*Measurement of standard deviation was performed through spreadsheet editor in Microsoft Excel.

Table 4

Heat deflection temperature (HDT) of Bio-PE and its blends.

It was observed that addition of PCL to Bio-PE promoted a subtle decrease of HDT in binary blends, being a reduction of approximately 3.9% for the Bio-PE/PCL (90/10 w/w), 9.3% for the Bio-PE/PCL (80/20 w/w) and 12.6% for the Bio-PE/PCL (70/30 w/w). This decrease is probably due to the addition of PCL in the compound, since it presents high flexibility, due to its low melting temperature ($\approx 60^\circ\text{C}$) and

glass transition temperature ($\approx 60^\circ\text{C}$); that is, the presence of PCL promoted a softening effect in Bio-PE, making it more flexible and thus diminishing HDT (França *et al.*, 2016; Moraes, 2016; Bezerra *et al.*, 2017b).

The addition of PEgAA promoted different trends in Bio-PE/PCL blends. It can be observed that for the ternary blends (90/10/10 and 70/30/10 w/w/phr), there is a behavior similar to

that presented by their respective binary blends. For Bio-PE/PCL/PEgAA (80/20/10 w/w/phr), there is an increase in HDT in relation to Bio-PE; this increase being approximately 4.9%.

In general, the individual contribution of each component and the morphology presented by the phases in polymer blends are the most important characteristics in the blend performance under HDT analysis.

Summing up, the continuous phase in a compound provides a greater contri-

bution to the HDT of polymer blends, since this is the blend matrix itself, as

also reported by Ferreira *et al.* (1997) and Luna *et al.* (2014).

Scanning Electron Microscopy (SEM) Images

Figures 2 to 8 show SEM images of Bio-PE, Bio-PE/PCL and Bio-PE/PCL/PEgAA. This analysis was performed on the fractured surfaces of the blends

after the impact strength. Images were also captured on samples submitted to phase extraction.

Bio-PE, where ductile fracture is observed on the surface of the Bio-PE due to the plastic deformation.

Figure 2 shows SEM images of

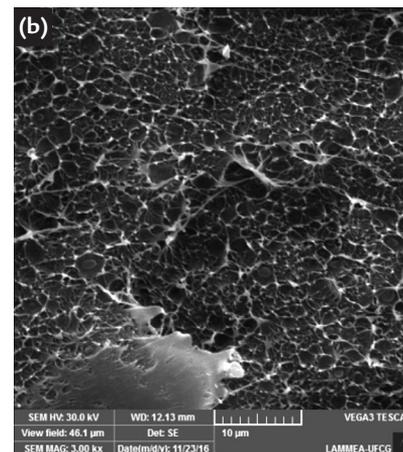
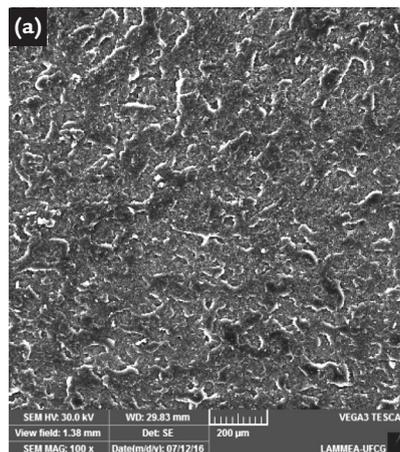


Figure 2
SEM images of Bio-PE at (a) 100x and (b) 3000x.

Figures 3, 4 and 5 (a) show SEM images of the Bio-PE/PCL blends at 90/10, 80/20 and 70/30, respectively.

they present a honeycomb morphology, as also reported by Roeder *et al.* (2012).

is, coalescence of PCL phase, which is indicated by the arrows. Additionally, there can be observed for the compound with 30% PCL, a greater number of pulled out particles (Bucknall and Paul, 2009; Liu *et al.*, 2011). Table 5 displays data for the average diameter of binary blends' dispersed phase.

The SEM images show typical morphology of immiscible blends, where Bio-PE and PCL phases have low affinity with each other and present well-defined borders. In addition,

With the overview of SEM images, it is verified that increase of PCL content in the binary blends (Bio-PE/PCL) provided an increase in the mean diameter of the dispersed phase; that

Composition	Average Diameter (μm)*
Bio-PE/PCL (90/10 w/w)	1.2±0.1
Bio-PE/PCL (80/20 w/w)	2.0±0.1
Bio-PE/PCL (70/30 w/w)	2.8±0.2

Table 5
Average diameter of binary blends' dispersed phase.

*Measurements were done using Tesca See 3 software. The average diameter was computed by the mean of twenty measurements.

SEM images of binary blends' dispersed phase extraction is presented in Figures 3b, 4b and 5b. Pores are identified

in these images as a result of extracted PCL. Therefore, as already observed, the extracted phase corroborates with the indicative

of being an immiscible system, reinforcing the other results discussed above herein (Passador *et al.*, 2008; Barra *et al.*, 2003).

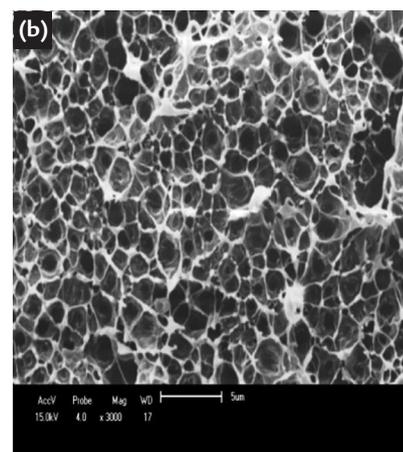
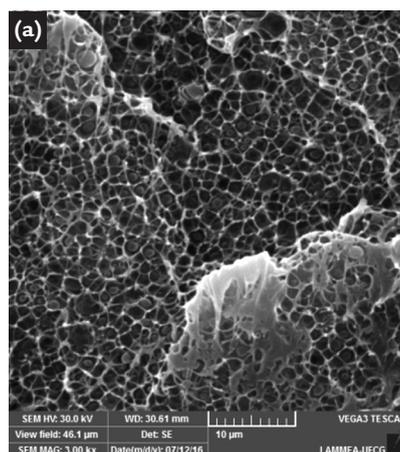


Figure 3
SEM image of Bio-PE/PCL (90/10) at (a) 3000x and (b) SEM image after dispersed phase extraction.

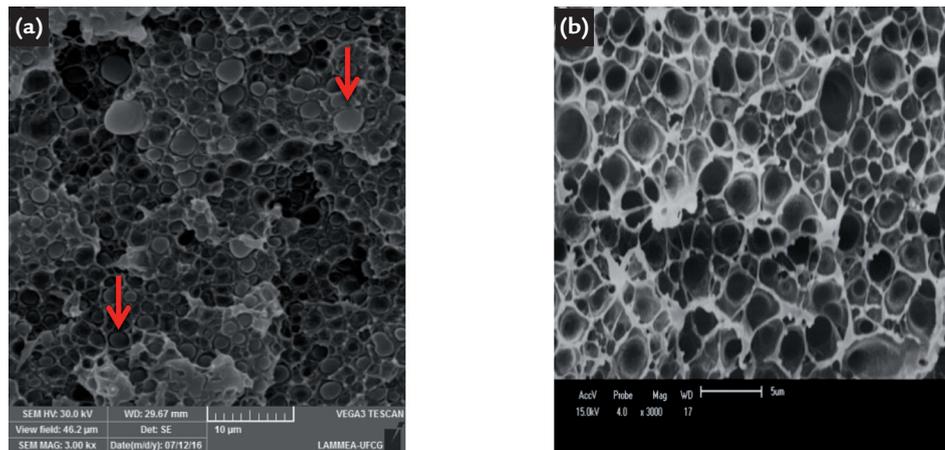


Figure 4
SEM image of Bio-PE/PCL (80/20) at (a) 3000x and (b) SEM image after dispersed phase extraction.

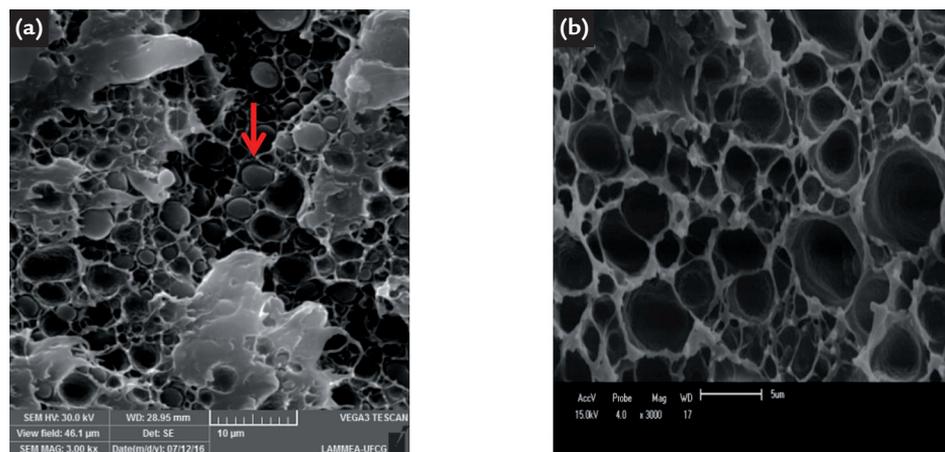


Figure 5
SEM image of Bio-PE/PCL (70/30) at (a) 3000x and (b) SEM image after dispersed phase extraction.

The effect of PEGAA on the phase structure of Bio-PE/PCL blends is shown in Figures 6 to 8. For the compositions Bio-PE/PCL/PEGAA (90/10/10 w/w/phr and 80/20/10 w/w/phr) (Figures 6 and 7), a quite similar morphology to that shown by Bio-PE can be observed. These SEM images display a homogeneous morphology, and it is difficult to distinguish the PCL dispersed phase in the Bio-PE matrix. This effect can be understood as a result of the PEGAA's diffusion and ability to remain at the interface, promoting a reduction of interfacial energy and avoiding the coalescence between the particles (Plochocki *et al.*,

1990; Pracella, 2016).

For Bio-PE/PCL/PEGAA (70/30/10 w/w/phr) (Figure 8), SEM images are similar to those verified for Bio-PE/PCL (70/30 w/w). Nevertheless, a smaller amount of pulled out particles are observed in relation to the binary blend. At this composition, PEGAA was less effective compared to Bio-PE/PCL/PEGAA (90/10/10 and 80/20/10 w/w/phr) compounds.

Addition of PEGAA increased the interfacial adhesion, due to the chemical interaction between the hydroxyl group of PCL and the acrylic acid group, as also reported by Bezerra *et al.* (2017a). Therefore, the incorporation of PEGAA provided a better ad-

hesion among the phases, decreasing the dispersed phase and contributing to the morphology stabilization of polymer blends compared to the non-compatible ones (Sánchez *et al.*, 2001, Moura *et al.*, 2008, Liu *et al.*, 2011, Pracella, 2016; Agrawal *et al.*, 2018). Table 6 displays data for the average diameter of ternary blends' dispersed phase.

SEM images of ternary blends after extraction of dispersed phase, showed pores due to PCL extraction, confirming PEGAA addition improved the homogeneity and affinity among the blend components (Barra *et al.*, 2003; Passador *et al.*, 2008).

Composition	Average Diameter (μm)*
Bio-PE/PCL/PEGAA (90/10/10 w/w/phr)	0.9 \pm 0.1
Bio-PE/PCL/PEGAA (80/20/10 w/w/phr)	0.9 \pm 0.2
Bio-PE/PCL/PEGAA (70/30/10 w/w/phr)	2.2 \pm 0.1

Table 6
Average diameter of ternary blends' dispersed phase.

*Measurements were done using Tesca See 3 software. The average diameter was computed by the mean of twenty measurements.

Figure 6
SEM image of Bio-PE/PCL/PEgAA
(90/10/10 w/w/phr) at (a) 3000x and (b)
SEM image after dispersed phase extraction.

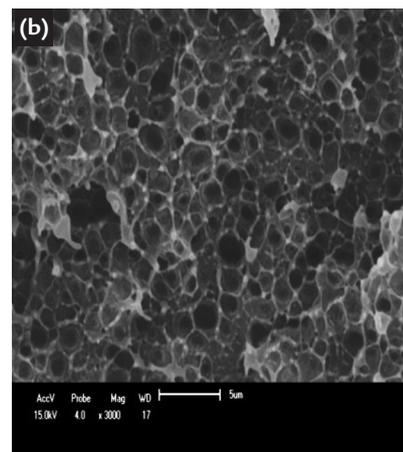
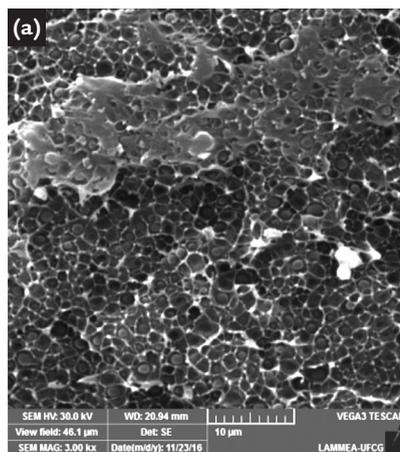


Figure 7
SEM image of Bio-PE/PCL/PEgAA
(80/20/10 w/w/phr) at (a) 3000x and (b)
SEM image after dispersed phase extraction.

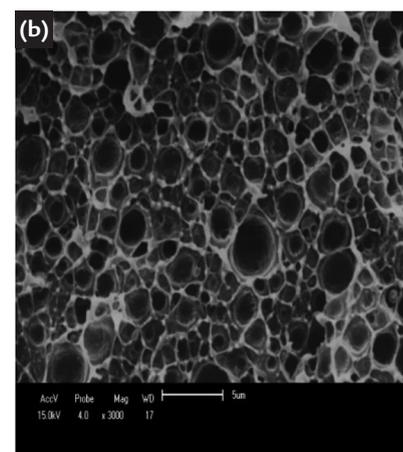
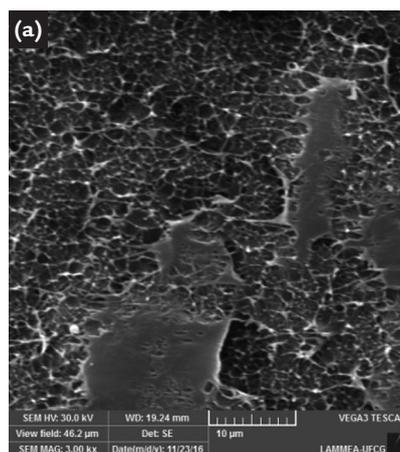
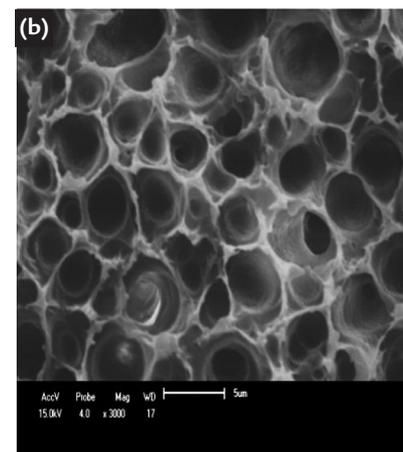
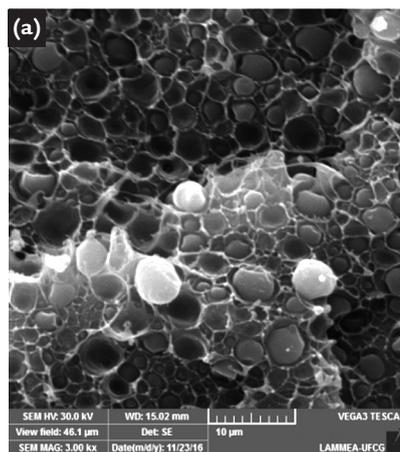


Figure 8
SEM image of Bio-PE/PCL/PEgAA
(70/30/10 w/w/phr) at (a) 3000x and (b)
SEM image after dispersed phase extraction.



4. Conclusions

Polymer blends were processed with Bio-PE and PCL upon addition of the functionalized copolymer PEGAA. Through XRD diffractograms it was observed the addition of PCL and PEGAA did not significantly change the diffraction patterns of Bio-PE. The presence of

PCL improved the impact strength of the blends. For the binary blends, addition of PCL conducted a slight decrease in HDT when compared to neat Bio-PE; however upon addition of PEGAA, the HDT increased. With the SEM images, it was verified that the methodology applied during

extraction was effective to remove PCL. Additionally, SEM images showed that addition of PEGAA significantly reduced the mean particle size, as well as the agglomeration and coalescence of the blends, the best results being verified for ternary blends at 90/10/10 and 80/20/10 w/w/phr.

Acknowledgements

The authors thank to Labmat (Laboratory of Materials Engineering/CCT/

UFCG), MCTI/CNPq, PDJ/CNPq, PNPd/CAPES and CAPES for financial support.

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Received: 22 February 2018 - Accepted: 25 February 2019.

