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RESEARCH ARTICLE OPEN ACCESS

BIODEGRADABLE POLYMERS BASED ON NATURAL CAROTENOIDS

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ABSTRACT

Carotenoids such as curcumin and bixin are polyisoprenoids, and are responsible for red, orange or yellow colors. Curcumin is a yellow hydrophobic polyphenol that presents a low molecular weight. Bixin is a natural color extracted from the Annato tree and its color varies from yellow to red due to the presence of the isomer carotenoid trans-bixin. Food and cosmetic industries use them due to their antioxidant properties. The biodegrading properties of polymer blends can be improved by the addition of vegetable oil, organic and inorganic additives or by mixing them with a biodegradable polymer. According to previous studies, polymers produced by a mixture of Moringa polymer (PMO), polyethylene (PE) and commercial biodegradable polymers (PB), composed of PBAT (poly(butylene adipate-co-terephthalate)/PLA (polylactic acid), presented mechanical properties similar to those of PE, except for a higher biodegradation capacity. Vegetable oils can be used as plasticizers for polymer blends and Moringa oil and improved the biodegradation properties in other studies.

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INTRODUCTION

In the last few decades, the world has awakened to the need for reducing the volume of solid waste produced by modern society. Plastic waste represents a significant part of that waste. Biodegradable polymers were developed but each one had a specificity for its complete degradability. Trade barriers in Europe and the United States have led other countries to apply standards that promote the production of sustainable and biodegradable materials. In the 2010s, some 23 states in Brazil prohibited the use of non-biodegradable plastic bags, while others indicated the use of oxo-biodegradable materials and others presented proposals for a gradual replacement. As of 2010, Brazilian plastic bags can be produced by using polymers as polyethylene, oxo-degradable polymers, biodegradable polymers and their blends. The market bags can be distributed for free and have been discarded in landfills without treatment or recycling. The literature presents biodegrading studies considering a biodegradation for virgin materials and disregarding the impact on the degradation capacity caused by the processing and additives necessary for the conformation of the final product. In previous studies, Finzi-Quintão and other authors studied the biodegrading behavior for blends of vegetable oils and plastic bags composed of polyethylene and biodegradable material. Due to this, blends of degradable and inert plastic bags with vegetable oils and their polymers were studied to improve the biodegradation behavior of polymers classified as bio inert materials. Studied blends show mechanical properties like commodity polymers such as polyethylene but with a higher biodegrading capacity (Finzi-Quintão *et al*. 2018; Finzi-Quintão, Novack, and Bernardes-Silva 2016; Novaes *et al*. 2018). Commercial polymers such as low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polystyrene (PS) and others are classified as bio inert materials (Poley *et al*. 2004; Rocha and Moraes 2015; Sunilkumar *et al*. 2012; Yashchuk, Portillo, and Hermida 2012). They are produced from petroleum and their high resistance to biodegradation is due to their long chain molecules(Ojeda *et al*. 2009; Ojeda and Camargo 2008). According to the theory of *microbial infallibility: "The organic compost may be degrading with appropriate environmental conditions"*(Jiao *et al*. 2010). Therefore, the theory indicates that biodegradable materials biodegrade only under ideal conditions. Polyethylene (PE) is a synthetic polymer derived from petroleum, which is used on a commercial scale for packaging products. PE presents a high chemical resistance, a good processability, a low cost

of production and a biodegrading resistance. PE is used in low- (LDPE) and high- (HDLPE) density configurations. LDPE presents 20,000–45,000 g.gmol^{-1} molecular weight (Mw) and a melting temperature (Tm) of 120-145 °C(Burlein and Rocha 2014; Finzi-Quintão *et al*. 2018; Matzinos *et al*. 2002; Selke *et al*. 2015). The degradation capacity of polymers derived from petroleum can be improved by adding pro-degradant additives based on metals such as manganese, iron and zinc. Oxo-degradation is promoted by these metallic additives due to the acceleration of the polymer oxidation, catalyzed by the presence of oxygen and light. The polymer chain fragments into small parts that allow the biological attack and favor a complete biodegradation (Contat-Rodrigo 2013; Kumar Sen and Raut 2015; Sunilkumar *et al*. 2012). Biodegradation processes may occur on different phases that can be separated in individual stages or in one single phase. The biodeterioration phase occurs by the activity of microorganisms as fungi and bacteria. The bio-fragmentation phase refers to a cleavage of the polymer chain due to the action of biotic or abiotic factors. The assimilation phase occurs when small pieces of the polymer can be transported into the cytoplasm of microorganisms to produce energy, biomass and metabolites(Gaines *et al*. 2015; Leja and Lewandowicz 2010; Wang *et al*. 2015). The biodegradation process can be quantified by the amount of carbon dioxide produced during the assimilation(Finzi-Quintão *et al*. 2016; Pagliano *et al*. 2017).

Biopolymers can be based on renewable or synthetic resources and produced by fermentative processes or by chemical reactions. Polylactic acid (PLA) and polyhydroxybutyrate (PHB) are biodegradable materials produced by a fermentative process and poly(butylene adipate-co-terephthalate) (PBAT), poly(ε-caprolactone) (PCL) and thermoplastic starch (TPS) are produced by a polycondensation reaction(Pagliano *et al*. 2017; Vieira *et al*. 2011; Yeh *et al*. 2010). PBAT is an aliphatic/aromatic copolyester, with Mw = 126,000 g.gmol^{-1} and Tm = 120–150 °C, that exhibits the best processability behavior when compared to similar biopolymers. It is a hydrophobic polymer that can be degraded under composting conditions, which is considered a good polymer to blend with PLA because it improves its processability(Brandelero, Grossmann, and Yamashita 2012; ElShafei *et al*. 2017; Hongdilokkul *et al*. 2015; Marinho *et al*. 2015; Wei *et al*. 2015). PLA is a thermoplastic polyester synthesized from L-lactide, with Mw = 180,000 g.gmol^{-1}, Tm = 130–180 °C, a low thermal stability during processing and low crystallization rates (Abdelwahab *et al*. 2012; Garrison, Murawski, and Quirino 2016; Gigante *et al*. 2019; Marinho *et al*. 2015; Matta *et al*. 2014; Patrício and Bártolo 2013; Ruellan *et al*. 2015; Weng, Jin, *et al*. 2013; Weng, Wang, *et al*. 2013; Yagi *et al*. 2014). The blend of petroleum polymers with biodegradable polymers increases their susceptibility to degradation and reduces the use of pro-degradant additives(Finzi-Quintão *et al*. 2018; Yashchuk *et al*. 2012). The blend of PLA with LDPE has a higher biodegradation capacity in comparison to LDPE. When LDPE was increased in the mixture, it lost its mechanical properties (Imre and Pukánszky 2013). There are several studies about blends of PLA with other polymers. PBAT is a co-polyester and it is biodegradable, hydrophobic and flexible, some properties that are similar to polyethylene (Marinho *et al*. 2015). The mixture of PBAT/PLA with LDPE is widely used to produce market bags due to their similar processability properties. According to literature, vegetable oils (VOs) can be used as pro degrading additives for conventional polymers, but they reduce their crystallinity and thermal resistance(Bicalho, Novack, and Melo 2011; Ojeda and Camargo 2008; Selke *et al*. 2015; Winkler and Warner 2008; Zainal *et al*. 2018). VOs are used as plasticizers and fillers for polymers. They are commonly used as plasticizers and fillers for polymers, as synthesizers of hydrophobic polymers and as a base for synthesizing polyurethane, polyester and polyolefins (Aguilera *et al*. 2016; Leveneur *et al*. 2014; Miao *et al*. 2014). VOs are triglycerides composed of several fatty acids, which are represented by esters of glycerol with three long chain fatty acids (Ain *et al*. 2017; Mizera *et al*. 2018; Mizera and Ryszkowska 2016; Ristić *et al*. 2012; Zainal *et al*. 2018). VOs are suitable for producing monomers with structures similar to petroleum and they can be polymerized according to chemical reactions as transesterification, reversible addition fragmentation chain transfer (RAFT), epoxidation reaction and thermal polymerization(Jiménez-Carvelo *et al*. 2017; Miao *et al*. 2014; Sinnwell and Ritter 2007; Stempfle *et al*. 2014). The microwave irradiation can be used as a thermal polymerization process and this technology is used in organic synthesis, presenting advantages as safety, speed, effectiveness and rate enhancement by selective heating (Aguilera *et al*. 2016; Chatti *et al*. 2006; Jovanovic and Faculty 2007; Da Porto, Decorti, and Natolino 2016; Yu and Liu 2007). Polymerization under microwaves (MW) irradiation is becoming common for the synthesis of polyesters, biodegradable polymers and ring open processes due to the increase of the reaction rates and the decrease of the reaction times that happens using this technique. In most studies, the reactions assisted by MW had a reduction in the reaction time and an increase in the reaction rate in comparison to conventional heating(Aguilera *et al*. 2016; Chatti *et al*. 2006; Gaines *et al*. 2015; Miyake, Yokomizo, and Matsuzaki 1998; Zhang, Liao, and Liu 2004). VOs can be extracted from seeds as castor oil, soybean, linseed and sunflower and they are commonly used to produce resins, monomers, polyesters and polyurethanes. *Moringaoleifera* oil (MO) can be extracted from seeds *of Moringa oleifera* Lam, which is a small tree native to northern India and it belongs to the Moringaceae family(Anwar *et al*. 2007; Bhutada *et al*. 2016; Da Porto *et al*. 2016; Rodríguez-Pérez *et al*. 2015; Tiloke *et al*. 2018; Tiloke, Phulukdaree, and Chuturgoon 2013). MO presents oleic acid as the fatty acid with a higher concentration (71%) and a high stability due to the presence of other unsaturated fatty acids that favor the polymerization process(Bhutada *et al*. 2016; Fakayode and Ajav 2016). The polymerization under MWs resulted in a *Moringa* polymer (PMO) that was mixed with LDPE (PE) and PBAT/PLA (PB), producing a PMO-PE-PB ternary blend with a high biodegradation capacity (Finzi-Quintão *et al*. 2017; Yu and Liu 2007).

Organic pigments can be used as additives to improve some material properties like biodegradation, antioxidation, antifungal and antibacterial properties. The main natural pigments are curcuminoids, riboflavins, caramels, carotenoids and inorganic pigments. Carotenoids are polyisoprenoids responsible for red, orange or yellow colors and show an extensive system of conjugated double bonds(Carlos Eduardo Rocha *et al*. 2012; Durães *et al*. 2006; Sellimi *et al*. 2015; STAFFA 2016). The basic carotenoid structure is symmetrical, linear and usually contains 40 carbon atoms, often with one or two cyclic structures at the end of their conjugated chains. Bixin and curcumin are pigments that present carotenoid compounds with antioxidant properties that are capable of sequestering free radicals(COLDEBELLA *et al*. 2014; Giménez *et al*. 2015; Sharma *et al*. 2017; Souza *et al*. 2016; Zia *et al*. 2016). Brazilian conditions are favorable to turmeric cultivation, which produces natural pigments called curcuminoids. Curcuminoids are pigments extracted from *Curcuma longa*, in which curcumin is the major constituent (Figure 1). Pure curcumin can be obtained by the crystallization of an oleoresin, followed by a recrystallization, to remove volatile oils and other plant extracts. The extracted pigment is insoluble in water and soluble in organic solvents(Bechtold and Mussak 2009; COLDEBELLA *et al*. 2014; Giménez *et al*. 2015; Laczkowski and Lackzkowski 2013; Volp, Renhe, and Stringueta 2009; Zia *et al*. 2016).

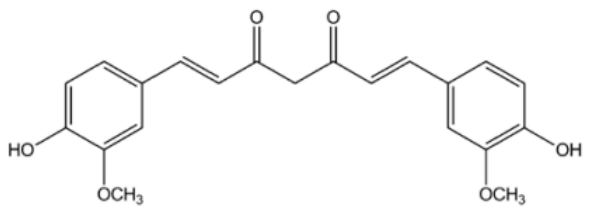

Figure 1. Curcumin structure [61]

Bixa orellana L.is a small tree, native to South America, which seeds are covered with a red resinous layer where the natural pigment can be obtained. The principal carotenoid in the *B. Orellana* seed coat is

known as bixin but there are small amounts of norbixin (Figure 2)(Souza et al. 2016; Volp et al. 2009). Bixin pigment is obtained from Annato(*Bixa orellana*) seeds using non-polar and aqueous alkali solvents [61,67,73–75]. The trans-bixin is an isomer which presents a red color and it is a fat-soluble pigment. *Annato* extracts show antimicrobial and antioxidant activities and curcuminoids show biological activities such as anti-inflammatory and antitumoral action(Augusta, Xavier, and Mercadante 2014; Carlos Eduardo Rocha et al. 2012; Fan et al. 2016; Giménez et al. 2015; Mercadante and Pfander 2001).

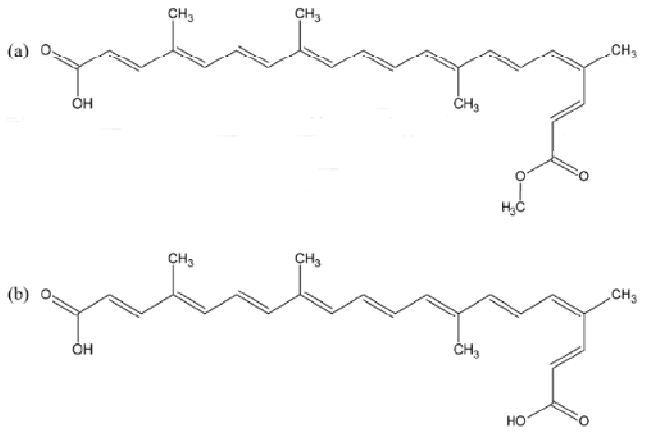

Figure 2. Bixin (a) e norbixin (b) structure [61]

Carotenoid pigments can be added to numerous food preparations and for textiles to give them yellow and red colors. These pigments can also be used on cosmetics formulations, tattoos and for medicinal purposes. Bixin and curcumin have been used as photosensitizers in organic solar cells and as an index of degrading food. As shown before, they show antimicrobial and antioxidant activities, biological activities, anti-inflammatory and antitumoral action. According to literature, *Moringaoleifera* oil and its polymer presented a plasticizer and biodegrading behavior when they were blended with commercial polymers (Finzi-Quintão et al. 2017; Rahmalia, Fabre, and Mouloungui 2015). Due to those properties, this manuscript presents a study about curcumin and bixin pigments used as additives for mixtures composed of PMO with PE and PB. This manuscript shows the influence of these pigments on thermal and mechanical properties of polymer blends and it also impacts on their biodegradation behavior.

RESEARCH ELABORATIONS

Samples Preparation: MO was extracted from Moringa seeds (Guanambi, Bahia, BR) for 19 hours in a Soxhlet extractor in the presence of hexane (1L, PA ACS, Synth, SP, BR). LDPE (PE) was obtained from transparent food bags and the PBAT/PLA (PB) from plastic bags bought in markets and hypermarkets (Belo Horizonte, MG, Br). The polymer's composition was characterized by the author in other works (Finzi-Quintão et al. 2017, 2016; Rahmalia et al. 2015). PMO was obtained by thermal polymerization of Moringa oil in a microwave oven (LabPol, CAP,UFSJ, OB, MG,BR), 850 W, for 16 h. The polymerization was monitored by iodine, peroxide and acidity tests. Bixin was extracted from annatto (red) and curcumin (yellow) from 5 g of curcuma seeds solubilized in 100 mL of hexane (LABPOL, UFOP, MG,BR). Polymer blends were produced by a mixture of PMO, PE and PB in presence of xylene under heating (180 ± 5 °C), colored with 5% in mass of carotenoids pigments ($P15_{pigment}$). When the mixture became a homogeneous liquid mixture, it was poured into molds (casting method) for solvent evaporation and sample drying. Ternary blends were composed of 15w% (weight) of PMO, 35 w% of PE and 50 w% of PB. This concentration was determined in previous studies (Finzi-Quintão et al. 2017; Poley et al. 2004). The control blend is composed of 50% of PE and 50% of PB (named PEPB).

The ternary blend was produced by casting, and dried for 48 h. Then, it was pressed by heating for 5 m at 145 °C until it presented 3 mm of thickness. Figure 3 shows ternary blends with curcumin ($P15_{curcumin}$), bixin ($P15_{bixin}$) and without pigments ($P15_{original}$).

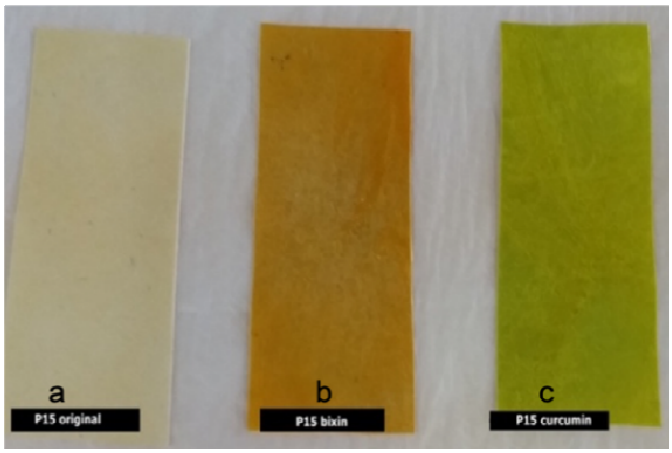

Figure 3. Images of P15 samples (a) $P15_{original}$ (b) $P15_{bixin}$ (c) $P15_{curcumin}$

Characterization Analysis: *Fourier transform infrared spectroscopy (FTIR) was performed by employing a FTIR System Spectrum (Model GX/Perkin Elmer, wavenumber range of 4000–400 cm^{-1}, mass: 2 mg sample, 600 mg KBr, UFOP, MG,BR).* Gel Permeation Chromatography (GPC) was performed by employing Shimadzu instrument (Model: LC-20AD, solvent: THF, column: 1 Waters linear e 1 Shimadzu GPC 803, flow: 1.0 $mL.min^{-1}$, injection: 20 µL, conc.: 0.2 % (p/v), UFRJ, RJ, BR).

Thermal gravimetric analysis with differential thermal analysis (TGA/DTA) was performed by employing a TA Instruments (model: SDT 2960 Simultaneous DTA-TGA model, 20 °C. min^{-1}, to 700 °C, on air atmosphere, UFOP, MG, BR). Scanning electron microscopy (SEM) was performed by employing a instrument (model: Jeol 1200 with EDS (energy-dispersive X-ray detector) (EDX) and wide X-ray fluorescence (WXRF), EDX 720/800HS, HV: 25.0 kV, det: SE, SEM MAG: 100x–4 kx, NANOLAB, UFOP, MG, BR). Crystallinity was performed by employing a RIGAKU (model: WXRD MINIFLEX-600 X-ray diffraction, Cu radiation (k=1,541å) , 40 kV , 20 mA, 20 °C, angles between 5°-60°, step of 0.025°, rate of 1°/min, UFSJ, MG, BR). The relative crystallinity was determined by the equation Xc = Ap/Ap+Ab, where Xc is the relative crystallinity, Ap is the total area under the diffractogram curve and Ab is the amorphous area. A tensile strength test was performed by employing an EMIC (model: DL-2000, Trd18, speed shift: 500 mm/min, load: 200 kgf, ASTM-D1708-13 method, UFOP, MG, BR). Controlled biodegradation analysis was carried out according to BrazilianStandardNBR 14283–1999 with Bartha respirometry: the equipment is shown in Figure 4 and its operation occurred according to Brazilian Standard NBR14283-1999. This standard specifies the biodegradation indexes (BI) for organic material present on waste disposed of on soil. BI is the amount of carbon dioxide produced during the biodegradation process by soil microorganisms in standardized conditions (Siracusa *et al*. 2008). Each respirometer must be prepared with 50 g of soil (humidity controlled between 50% to 70%) disposed (Figure 4F) in an Erlenmeyer flask (Figure 4G). On the side arm, (Figure 4D) 10 mL of KOH (0.2 N) solution was deposited using the Cannula with cannon Luer (Figure 4B and Figure 1E), closed with the cannula cap (Figure 4A). The KOH solution reacted with the CO_2 produced by the residue's biodegradation, forming K_2CO_3, used in titration of CO_2. Before closing the system, pressure was passed through an Ascarite filter (Figure 4J) for 5 m, maintaining the cannula cap open. The Ascarite filter prevents the passage of CO_2 and cleans the system of CO_2. For the closed system, NBR indicated the following sequence: first, close the cannula cap; second, close valve 1 (Figure 4H); and in the third step rubber stop (Figure 4H). Bartha respirometer must be in a temperature-controlled greenhouse (28 ± 2 °C) until the CO_2

production completely stops. Systems with residues/soil and the controller (soil) systems were provided in triplicate.

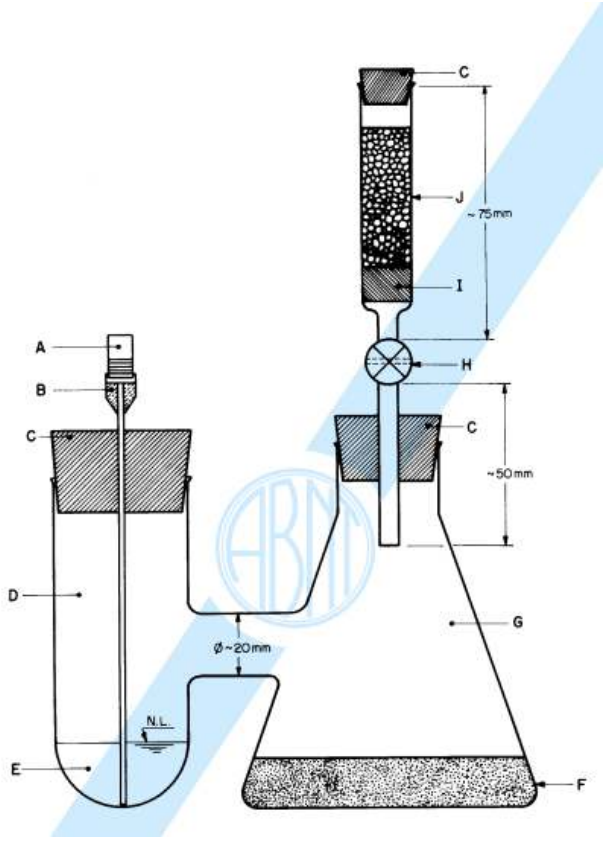

Figure 4. Bartha respirometer (A—cannula cap; B—cannula (Øi between 1 mm and 2 mm) with cannon Luer; C—rubber stopper; D—side arm (Ø 40 mm ~ H ~ 100mm); E—KOH solution; F—soil; G—Erlenmeyer flask (250 ml); H—valve I—support (glass or cotton wool); J—ascarite filter (Ø 15 mm ~ H ~ 40mm)) [79]

The titration of K_2CO_3 started 15 days after the respirometers were incubated in the temperature-controlled greenhouse. The solution presented in an Erlenmeyer flask was discarded and substituted by 10 mL of KOH (0,2 N). In this manuscript, the results after 14 weeks of a biodegradation test on a Bartha respirometer are presented. Day to day, the solution of K_2CO_3 was titrated to determinate the BI for polymeric residue. According to NBR, CO_2 and biodegraded carbon are calculated by the equations below. The CO_2 production was calculated for the soil/residue respirometer (Equation 1) and for the controller system (Equation 2) (A: measure of HCl 0,1 N used for controller's titration (mL); B: measure of HCl 0,1 N used for respirometer solution's titration (mL); 50: conversion factor for CO_2; f_{HCl}: conversion factor for HCl (0,1 N). CO_{2b} production due to biodegradation was calculated by the difference between the systems (Equation 3).

$$mol(CO_{2\,(soil/sample)}) = (A-B) \times 50 \times f_{HCl} \quad (1)$$

$$mol\,(CO_{2\,(soil\ control)}) = (A-B) \times 50 \times f_{HCl} \quad (2)$$

$$mol\,(CO_{2b}) = mol\,(CO_{2\,(soil/sample)} - CO_{2\,(soil\ control)}) \quad (3)$$

According to NBR, 50% of biodegraded carbon was converted to CO_2 and 50% was incorporated on soil as biomass and due to this, the carbon is effectively biodegraded (eq. 4).

$$C_b\,(mol\ C) = 2 \times CO_{2b}\ mol\,(CO_2) \quad (4)$$

NBR14283-1999 standard indicates the procedures to determine the biodegradation behaviour based on CO_2 production under controlled ambient for 14 weeks. According to NBR, residues which reduced more than 30% of mass under controlled respirometry producing, cumulatively, CO_2 can be considered degradable and mineralized when C_b is constant. Free biodegradation tests were carried out for 0,6 g of samples, buried in 1,500 cm^3 of compostable soil for 180 days, according to ASTM D5988–18. After this time, samples were weighed to verify the loss of mass.

RESULTS DISCUSSIONS

Moringa polymer was used on polymer blends as a plasticizer and biodegrading fill. PMO was produced from *Moringa* oil (MO) using thermal polymerization assisted by microwaves irradiation. GPC technique showed that MO's molecular weight (Mw) increased from 1214 $g.mol^{-1}$ of PMO's Mw to 50,000 $g.mol^{-1}$. FTIR analysis for MO and PMO confirmed the polymerization, indicated from the GPC result by the loss of MO bands at 1641cm^{-1} (double bonds) and 1427 cm^{-1}(C=O) (Figure 5). The polymerization process eliminates the double bonds and the carbonyl group due to the chain growing. According to Finzi-Quintão (Finzi-Quintão et al. 2017), PMO shows a plasticizer behaviour on ternary blends which did not present new structures on the FTIR analysis.

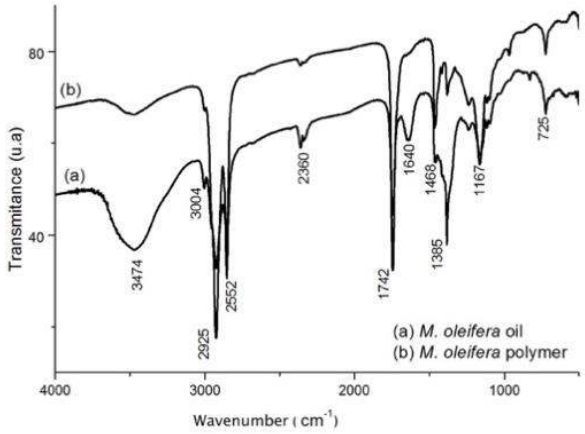

Figure 5. Fourier transform infrared (FTIR) spectra of *Moringaoleifera* oil and *Moringaoleifera* polymer

According to previous studies, the thermogravimetric analysis (TGA) of $P15_{original}$ presents a higher thermal resistance enhancement than that observed in PMO and PEPB [60]. Differential thermal analysis (DTA) for $P15_{original}$ indicated the compatibilizer effect of PMO on a PEPB. PE interaction with PMO was presented in the oxidation phase at 491 °C and the association of PEPB with PMO occurred at 442 °C. According to previous study, the oxidation temperature occurred at 254 °C which indicated the interaction between PLA and PBAT(Al-Itry, Lamnawar, and Maazouz 2012, 2014; Jr, Magalhães, and Oliveira 2013; Marinho et al. 2015; Yeh et al. 2010). $P15_{curcumin}$ lost its thermal resistance at 250 °C (Figure 6), presenting two thermal degradation stages. According to literature, pure curcumin has its first degradation temperature occurring between 205°C and 441 °C and its second degradation temperature between 441 °C and 630°C(Jr et al. 2013). $P15_{curcumin}$ presents the first interval of degradation between 270 °C and 300 °C and second between 300 °C and 400 °C and the third close to 400°C. Curcumin presents aromatic rings at the ends of the chain, which interact with the biodegradable part of $P15_{original}$, changing its interval of degradation. Thermal analysis showed that $P15_{bixin}$ presented a similar thermal resistance to $P15_{original}$ due to the interaction of the pigment with the biodegradable phase of $P15_{original}$.. Bixin's degradation curve presents a first degradation at 205 °C and a second between 210°C and 460 °C(Carlos Eduardo Rocha et al. 2012; Mercadante and Pfander 2001; Silva et al. 2005; Volp et al. 2009)and $P15_{bixin}$ starts the degradation close to 300 °C and shows a second phase of degradation at 450 °C. The structural chain was investigated by diffractometry, and the results showed that the samples changed their crystallinity when the dyes were added on $P15_{original}$ (Figure 7).

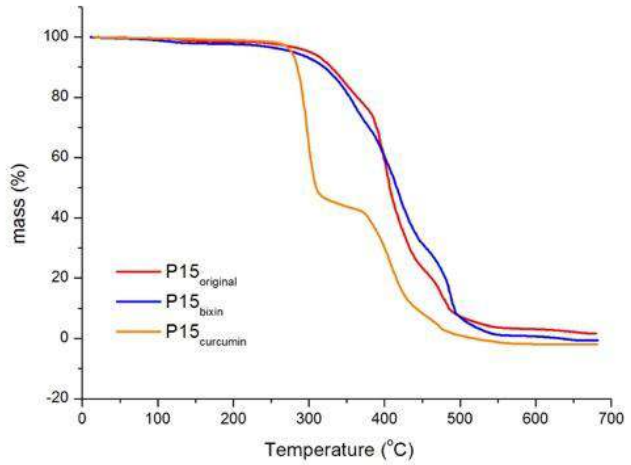

Figure 6. Thermogravimetric analysis (TGA) for $P15_{original}$, $P15_{bixin}$, $P15_{curcumin}$.

According to diffractograms, looking for 2Θ close to 21°, bixin improved the intensity of the peak 20 times while curcumin improved close to 200 times. The diffractogram of the pigmented samples shows the interference of carotenoids on ternary mixture structure due to the presence of functional groups (=O and –OH) which interact with biodegradable structures (PB and MO) present in ternary mixture. The ternary blends' diffractograms indicates a higher chain organization when they were pigmented with bixin and curcumin, leading to the consideration that the dyes act as nucleating agents.

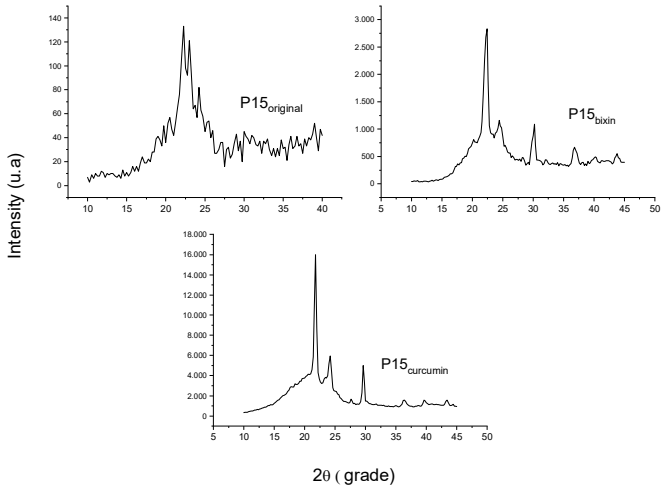

Figure 7. Diffractograms for samples $P15_{original}$, $P15_{curcumin}$ and $P15_{bixin}$

According to literature, PEPB mixtures lose less than 10% of their weight when submitted to the Bartha respirometer [3,79]. Curcumin is an antioxidant pigment and for the biodegradation test using Bartha Respirometry $P15_{curcumin}$ it showed less CO_2 production than $P15_{original}$, which is close to 30 mgCO_2. The curcumin addition reduced the biodegradation capacity of $P15_{original}$ whilst Bixin dye enhanced up to 36 mg CO_2 with a similar loss of weight (Table 1). After 14 weeks as described by the respirometer Brazilian standard, the original and bixin samples' loss was close to 30%, and that indicates biodegradation. However, curcumin presented a smaller biodegradation capacity. Biodegradation tests on respirometers were continued aiming to verify how the samples were affected by biodegradation. Therefore, after 35 weeks the respirometers were opened and $P15_{original}$ and $P15_{bixin}$ lost close to 85% of their mass whilst $P15_{curcumin}$ lost less than 20%. The samples were not mineralized due to the polyethylene presence, but they presented a significant degradation up to 35 weeks. Bixin did not improve its biodegradation behaviour from the original sample and curcumin presented antioxidant behaviour.

Table 1. Results for biodegradation process using Bartha respirometry and free test

Sample	Free test	Bartha Test 14 weeks		Bartha test 35 weeks	
	% *	% *	CO_2 (mg)	% *	CO2 (mg)
$P15_{original}$	51	27	114.03	82	312.02
$P15_{curcumin}$	57	22	80.56	62	120.03
$P15_{bixin}$	59	29	150.90	85	380.60

*weight loss

Samples submitted to the Bartha respirometer did not fragment after 14 weeks (Figure 8) but they lost weight and this has proved the biodegradation by CO_2 production. Therefore, only after 35 weeks, the samples presented a significative fragmentation behaviour because the biodegradation for samples with dyes occurred based on the CO_2 production. The respirometry was carried out under a controlled atmosphere and the free biodegradation test was not. The free biodegradation test was carried out based on samples under compostable soil for 6 months or 24 weeks resulting in loss where, like the Bartha tests (Table 1) and those samples, it did not fragment (Figure 9). Even for the respirometer, samples were analyzed after 35 weeks and they did not present a significant loss, it was a loss of 10 % of mass, and the sample turned thin. The complete fragmentation occurred after up to 70 weeks for bixin and 80 weeks for curcumin.
According to NBR 14283/99, 14 weeks would be enough to analyse the samples; however, tests were continued up to 35 weeks, when samples reduced up to 80% in their mass, indicating that PMO and PB fractions of samples were completely fragmented but not completely mineralized. Curcumin and bixin pigments presented a similar behaviour for the biodeterioration phase. Bixin presented the best results of microorganism's assimilation due to higher production of carbon dioxide.

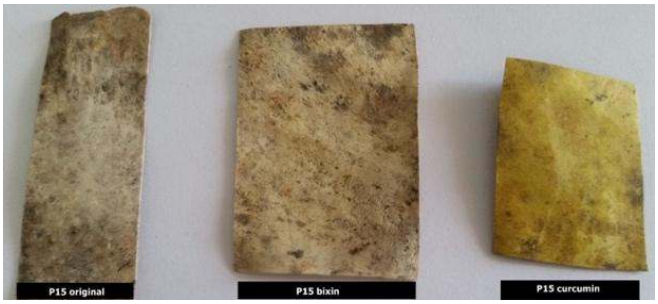

Figure 8. P15 samples after 14 weeks on Bartha respirometry

Figure 9. P15 samples after 180 days in free biodegradation test

The SEM micrograph before (Figure 8) and after biodegradation tests (Figures 9–13) showed that $P15_{curcumin}$ is less degraded than the other samples. The micrograph of the Bartha respirometer test confirmed the results obtained for mass production of CO_2. The micrograph showed that $P15_{original}$ and $P15_{bixin}$ were more degraded than $P15_{curcumin}$. The micrograph of $P15_{original}$ after the Bartha respirometer test showed structures similar to fibbers which would indicate an improvement in crystallinity. The micrographs for free biodegradation tests of $P15_{original}$ (Figure 11) and $P15_{bixin}$ (Figure 12) show a similar destroyed surface. The $P15_{curcumin}$ micrograph (Figure

13) for free biodegradation tests shows less surface degradation even losing the same mass percentage (Table 1). Considering the Bartha test, $P15_{original}$ micrograph shows a higher surface degradation (Figure 11) when compared to $P15_{bixin}$ (Figure 12). The $P15_{curcumin}$ shows the worst degradability behaviour. Contrary to the initial proposal to improve the degradability behaviour for a ternary sample with natural pigmentation, the results showed that is possible to use then to control the biodegradation.

According to literature, curcumin is a potent antioxidant which prevents free radicals production due to its chemical structure(Codevilla et al. 2015; Giménez et al. 2015; Santos and Souza 2017; Zia et al. 2016). Bixin also has an antioxidant effect and acts in reducing the formation of hydroperoxides in triacylglycerides oxidized by light (Carlos Eduardo Rocha et al. 2012; Mercadante and Pfander 2001; Rahmalia et al. 2015; Silva et al. 2005; Souza et al. 2016; Zhang and Zhong 2013).

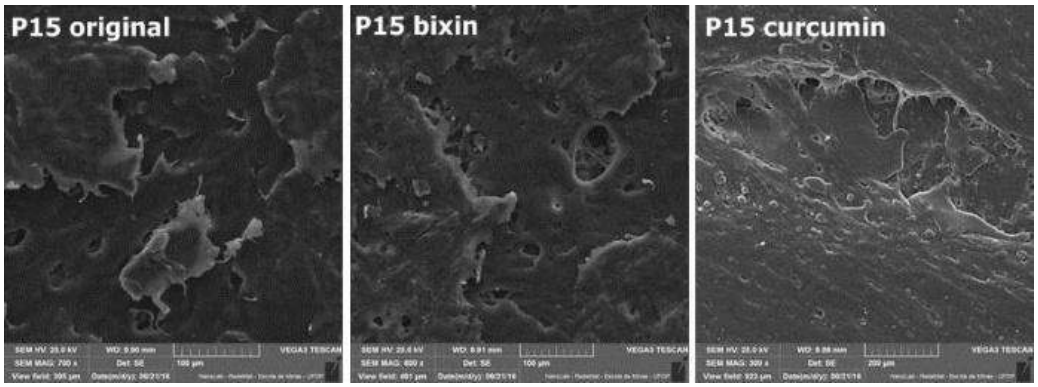

Figure 10. Micrograph of samples before biodegradation (SEM HV 20.0 kV) [$P15_{original}$ (SEM MAG: 700x); $P15_{bixin}$ (SEM MAG: 400x); $P15_{curcumin}$ (SEM MAG: 300x)]

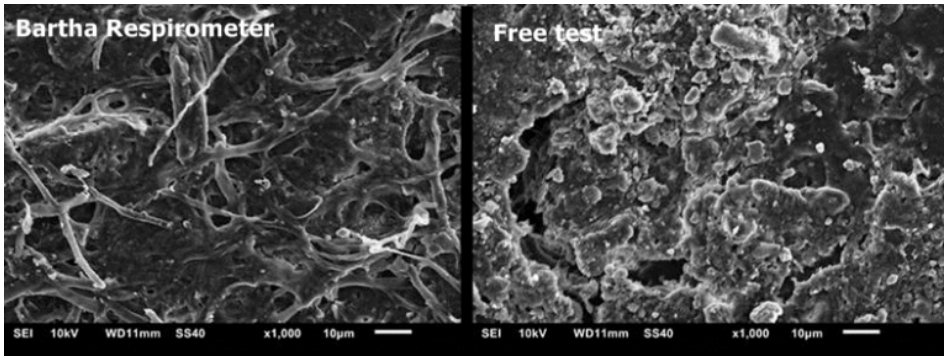

Figure 11. Micrograph of $P15_{original}$ after biodegradation tests

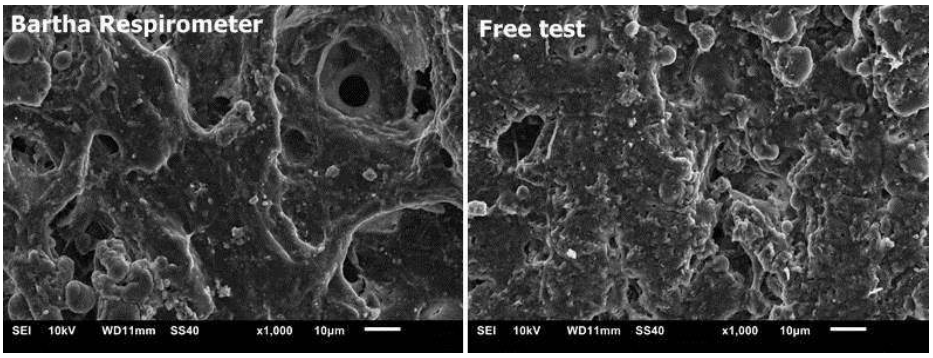

Figure 12. Micrograph of $P15_{bixin}$ after biodegradation test

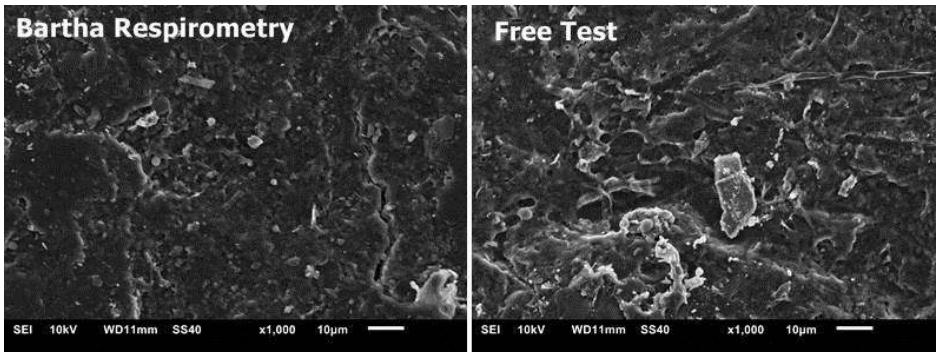

Figure 13. Micrograph of $P15_{curcumin}$ after biodegradation test

Curcumin stabilized the ternary mixture, delaying the biodegradability effect on the ternary mixture. $P15_{bixin}$ Raman spectrum shows characteristic bands of bixin carotenoid, defined at 1532 cm^{-1} (v1 C=C), 1154 cm^{-1} (v_2 C–C) e 1008 cm^{-1} (v_3 C–CH_3) (Figure 14). P15curcumin spectra are defined by vibrations at C=C (1528 cm^{-1}) e C–C (1167 cm^{-1}) for crocetin carotenoid (Figure 15). Raman spectra were used to verify and confirm diffractogram results that indicated a higher crystallinity of curcumin when compared to bixin.

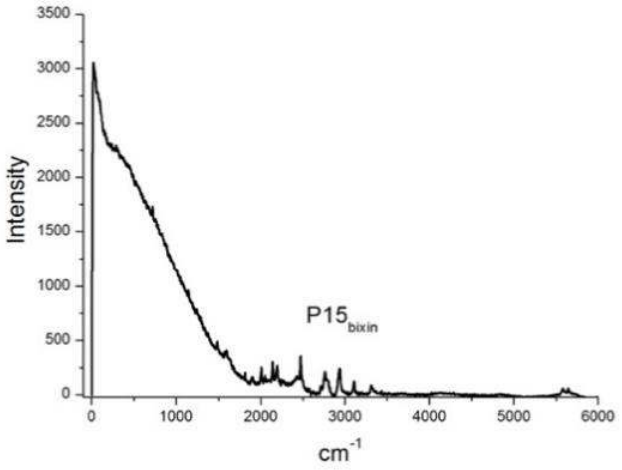

Figure 14. Raman spectra of $P15_{bixin}$

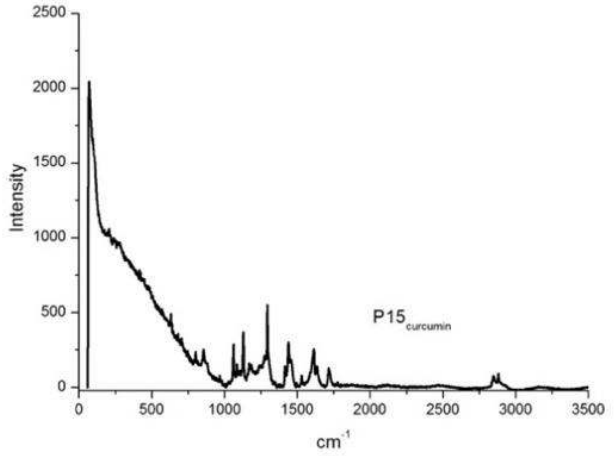

Figure 15. Raman spectra of $P15_{curcumin}$.

Table 2 shows the results of the tensile stress test for pigmented and non-pigmented samples. PMO addition reduced the stiffness of the PEPB sample but presented a similar tensile stretch. The curcumin presence indicated that the Young's modulus was recovered and that the tensile stress was reduced, and the bixin presence indicated a strong reduction on stiff and tensile stretch. The samples pigmented with bixin lost some mechanical properties. Meanwhile, curcumin presented a similar mechanical behaviour when compared to the original sample. Even with a reduction in tensile stress of the pigmented ones, the results were highly satisfactory because pigmented composites were produced with a higher biodegradation capacity and similar mechanical properties. According to tensile stretch, the presence of curcumin reduced the mechanical resistance of $P15_{original}$, while it improved the elasticity modulus and reduced the Young's modulus. The use of those natural pigments was not an advantage for mechanical resistance and biodegradation behaviour.

Carotenoids pigments reduced the tensile stress close to 30%, while slightly increasing the elasticity for ternary blends pigmented with curcumin and hard reduction for blends with bixin. The micrographs of samples before biodegradation tests and their diffractograms did not indicate significant morphological and structural changes that were caused by pigmentation. Bixin dye did not promote significant changes on thermal stability on $P15_{bixin}$; however, curcumin promoted a considerable decrease in thermal stability. Despite the fact that Raman spectra suggests a greater interaction between curcumin and the $P15_{original}$ polymer chain, the bixin addition decreased significantly the stiffness of the material, which impacts in its higher biodegradation capacity.

Table 2. Results oftensile strength test (ASTM-D1708-13)

Sample	Tensile stress (MPa)	Young modulus (MPa)	Elongation (%)
PEPB	8.74 ± 1.80	103.0 ± 3.1	23 ± 3
$P15_{original}$	9.21 ± 2.10	51.3 ± 1.6	17 ± 2
$P15_{curcumin}$	6.87 ± 1.80	67.0 ± 2.8	14 ± 3
$P15_{bixin}$	5.23 ± 1.20	19.0 ± 8.4	15 ± 3

CONCLUSIONS

Curcumin and bixin control the biodegradation capacity of ternary mixtures without a loss of mechanical properties from the original mixture. Curcumin is a potent antioxidant which prevents free radicals' production due to its chemical structure. Itstabilized the ternary mixture, delaying the biodegradability effect on it. Bixin also has an antioxidant effect that acts reducing the hydroperoxides formation but does not improve or delay the original degradation. However, curcumin reduces the thermal stability of the samples. Bixin dye did not impact on the thermal properties of polymer mixtures and it presented a higher biodegradation behaviour. The ternary mixture pigmented with curcumin lost thermal properties but improved the degradation control.

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