STUDY OF FLEXIBLE FILMS PREPARED FROM PBAT/PLA BLENDS REINFORCED WITH BIO-CACO$_3$

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Abstract: Plastics global annual production exceeds 250 million tons and more than 40 % of the total plastic production is used as packaging materials. The most widely used materials include polyethylene (PE) and polypropylene (PP), among others. However, petrochemical-based conventional packaging materials are non-biodegradable and cause serious environmental problems. Poly (lactic acid) (PLA), a linear aliphatic polymer is known as a biodegradable thermoplastic polymer with widely potential applications. However, its high brittleness and low toughness limits its application; blending PLA with PBAT (Poly (butylene adipate-*co*-terepthalate), an aliphatic-aromatic copolyester, was the solution found due to its high toughness and biodegradability. Nevertheless, differences between PLA and PBAT solubility parameter values lead to the formation of immiscible blends as well as reduction in their mechanical performance. CaCO$_3$ from avian eggshells, when added in PLA / PBAT composites imparts optimization of mechanicals properties due to its characteristic as reinforcing filler. This study aims to evaluate the effects of PLA addition in PBAT/PLA blends especially concerned to mechanical and thermal properties of PLA / PBAT / CaCO3 flexible films. Composites were prepared by melt processing, using a twin-screw extruder (L/D - 25). Before blown film processing, the composites were cooled down for a better dimensional stability, pelletized and dried at 60 ± 2 ºC for 24 h. The mechanical and thermal properties of obtained films were investigated by tensile tests, DSC and TG / DTG. In addition, the morphology of blends and composites were also evaluated by XRD and SEM analyses. The results showed important increase in crystallinity and tensile strength at break of flexible films without severe loss in elongation percentage, due to CaCO3 additional in PBAT / PLA blend with higher PLA contents.

Keywords: PLA, PBAT, CaCO$_3$, tensile tests, SEM.

1. INTRODUCTION

The large-scale production and consumption of plastics has created several problems worldwide: reduction of oil resources increased CO$_2$ discharge into the atmosphere and environmental pollution caused by waste plastics. Polymers are vastly employed for numerous purposes in different industrial segments [1], generating enormous quantities of discarding in the environment. Amongst the various components of waste in landfills, polymeric materials composites account for an estimated from 20 to 30% of total volume of solid waste disposed.

Sustainable use of resources associated to pollution prevention will be fundamental for next generations; needs toward both renewable and non-renewable feedstock management is crucial. One of the most concerned feedstock is fossil, normally used for energy and as an intermediate for petrochemical industries, including plastics; most of the conventional plastics are generally fossil-

based, capable to be accumulated in the environment after usage as solid wastes. An alternative approach to replace non-biodegradable or/and fossil-based plastics is the use of bio-based ones.

So, much endeavor has been committed to developing biodegradable and renewable resource–derived polymers; as the world moves toward the production of sustainable environmentally friendly plastics (bio-plastics), the production of biodegradable polymers has become more and more an area of relevant scientific interest [2].

Poly (lactic acid) (PLA), a linear aliphatic polymer, is a biodegradable thermoplastic polymer with widely potential applications [3], due to a number of interesting properties including biodegradability, biocompatibility, high strength and high modulus. For these reasons, PLA is a strong candidate for producing packaging materials; however, its high brittleness and low toughness limit its application [4]. PLA can be manufactured from biomass materials, such as cornstarch or beet sugar [5]; nevertheless, its elongation ability, impact strength, shock absorbance, toughness, physical aging and heat deflection properties are unsatisfactory for practical applications [6].

Blending PLA with other biodegradable polymers presents a more practical and economic measure to obtain a final product with properties not currently attainable. PLA/Poly (butylene-adipate-co-terephthalate) (PBAT) blends have been extensively investigated by many researchers [7 - 10] especially due to PBAT flexibility. In addition, PBAT is considered a good candidate for improving PLA toughness, besides being fully biodegradable and flexible aliphatic-aromatic copolyester designed for film extrusion and extrusion coating. Its most attractive feature is its high elongation at break [11].

Eggshell is a relevant waste material by-product of poultry industries and domestic kitchen waste. Currently, egg production throughout the world is 65.5 million metric tons per year, with Asia as a key contributor to global egg output growth [12]. By taking 11% of the weight, nearly 7.2 million tons of eggshell waste is created every year and if unutilized poses a potential pollution problem. Therefore, resourceful utilization of this waste is of great importance for reducing the environmental impact and for attaining higher profits. Eggshell is a natural bio-ceramic composite with an unique chemical composition of high inorganic (95% of calcium carbonate in the form of calcite) and 5% of organic (type X collagen, sulfated polysaccharides) components; this eggshell characteristic structure combined with substantial availability makes eggshells a potential source of bio-fillers efficiently used in polymer composites [13]. Bio - $CaCO_3$ was selected in this study since it yields a cost reduction in polymer blends and contributes for improving mechanical properties.

The proposal of present work is the development of flexible films from PLA / PBAT blends reinforced with bio-$CaCO_3$ from eggshell to foster improvement in tensile properties. Investigations in crystallinity will be performed by DSC analyses and thermal behavior accomplished by TG / DTG tests will indicate maximum degradation temperature and resulting mass loss. Scanning Electron Microscopy (SEM) will study blends morphology pointing toward phase miscibility between PLA and PBAT. X-Ray diffraction analyses will show interaction among all components involved.

2. EXPERIMENTAL

2.1 Materials:

The materials used in this study are listed below:

PLA type GS PLA AD 92W, from Mitsubishi, and PBAT type Ecoflex – FS, Basf; both were dried at 60 ℃ for 12 h before processing.

Avian eggshell white chicken were subjected to a thorough cleaning using tap water for removing of internal membranes and after kept for 4 h in a 100 ℃ water bath and finally dried at 100 ℃ for 2 h in an air-circulating oven. Eggshells were size reduced to 75 μm, by using ball mills and granulometric sieve and dried again in same condition, prior to be used.

Irgafos 168 and Irganox 1010, antioxidant from Basf: a synergistic blend, 0.1 % each one used to provide a processing and long-term thermal stabilizer system.

2.2 Preparation of blends and composites:

Composite materials were prepared according to Table 1. They were first processed by melting extrusion process, using a twin-screw extruder Haake Rheomex L / D - 25, temperature profile from feed zone to die 120 ºC to 145 ºC, 50 rpm screw speed and extrudates air-cooled before pelletizing.

Table 1: Designation and composition of blend and composite (phr = per hundred resin).

Materials	PLA (wt %)	PBAT (wt %)	CaCO$_3$ (wt %)	Irgafos 168 /Irganox 1010 (phr)
PLA/PBAT	50.0	50.0	---	0.1
PLA/PBAT	30.0	70.0	---	0.1
PLA/PBAT/CaCO$_3$	50.0	50.0	15.0	0.1
PLA/PBAT/CaCO$_3$	30.0	70.0	15.0	0.1

Blends and composites listed in Table 1 were processed in a single screw extruder Haake Rheomex, 48mm annular die, 140 ºC barrel temperature, BUR 2.0: 1, 14 rpm. Films average thickness =167 microns (or 0.17 mm).

2.3 Characterization:

Mechanical tests

Samples were analyzed in an Instron Equipment model 5567, 1 kN load cell, 500 mm.min^{-1}cross-head speed, room temperature. The specimen dimension was 130 x 25 mm^2 denoting respectively the length and breadth. Assessments were accomplished as per ASTM D882-02 [14].

Differential Scanning Calorimetric Analysis

Thermal behavior was examined in a DSC Mettler Toledo apparatus, ASTM D3418-08 [15]. Samples were heated from 30 ºC to 300 °C, kept at 300 ºC for 10 min and after cooled down to 30 °C, 10 °C . min^{-1} and further heated back to 300 °C at 10 °C . min^{-1}. The percent crystallinity was calculated upon the second heating by using Eq.1 based on Hermans and Weidinger equation [16]:

$$X_c\ (\%) = \frac{100 * \Delta H_m - \Delta H_{cc}}{f * \Delta H_{m\infty}} \tag{1}$$

Where "Δh_m" is the measured heat of fusion, Δh_{cc} the cold crystallization enthalpy (j.g^{-1}), "f" is the weight fraction of PLA or PBAT in the blend and "$\Delta h_{m\infty}$" is the enthalpy of fusion for a crystal having infinite crystal thickness (93 j.g-1 for PLA and 114 j.g-1 for PBAT).

Thermogravimetric analyses (TG)

Thermogravimetric analyses provides complimentary and supplementary characterization information to DSC, by measuring the amount and rate (velocity) of change in the mass of a sample as a function of temperature or time in a controlled atmosphere. Measurements are used primarily to determine the thermal and/or oxidative stabilities of materials as well as their compositional properties. The technique can analyze materials that exhibit either mass loss or gain due to decomposition, oxidation or loss of volatiles (such as moisture). TG were performed using a DSC Mettler Toledo apparatus, according to ASTM - E 1641 – 07 [17], by using 5 – 9 mg of sample, within a 25 ºC to 600 ºC program, at a $10°C.min^{-1}$, in a nitrogen flow of $50\ ml.min^{-1}$.

Scanning Electron Microscopy

Investigations were accomplished in a Hitachi-table top TM 300 microscope, for an investigation of morphology, in various magnification micrographs. Acceleration voltage of 10 kV was used to collected SEM images of sample. The samples were freeze - fractured in liquid nitrogen and coated with gold before analysis.

XRD (X - RAY Diffraction Analysis)

It was used a X - Ray diffractometer, Rigaku Multiflex, 40 KV, 20 mA, scanning 5 to 60 °, 2 θ, step 0.02 °, 2 θ, $1\ °C.min^{-1,}$ continuous analysis. It provides, among other, information on samples crystallinity, via diffractograms.

3.   RESULTS AND DISCUSSION

Mechanical properties of PLA / PBAT blends and composites are summarized on Table 2:

Table 2: Tensile properties results of PLA / PBAT blends and composites.

Blends and composites	Tensile Strength (MPa)	Elongation at Break (%)	Young´s Modulus (MPa)
PLA / PBAT (50.0 / 50.0)	18.0 ± 0.7	880.0 ± 26.1	68.6 ± 1.5
PLA / PBAT (30.0 / 70.0)	16.0 ± 0.3	890.0 ± 54.7	42.5 ± 0.8
PLA / PBAT / $CaCO_3$ (50.0 / 50.0 / 15.0)	27.5 ± 1.2	280.0 ± 72.1	110.0 ± 0.9
PLA / PBAT / $CaCO_3$ (30.0 / 70.0 / 15.0)	4.0 ± 0.6	380.0 ± 83.5	34.7 ± 0.7

In Table 2 values obtained for Tensile Strength, Elongation at Break and Young´s Modulus for PLA / PBAT (50.0 / 50.0) and PLA / PBAT / $CaCO_3$ (50.0 / 50.0 / 15.0) showed higher results than those ones obtained for PLA / PBAT (30.0 / 70.0) and PLA / PBAT / $CaCO_3$ (30.0 / 70.0 / 15.0). A higher PBAT concentration in these latter blends contributed for reducing $CaCO_3$ miscibility in prejudice of tensile properties.

Detailed behavior of investigated PLA / PBAT blends and composites is presented in diagram stress-strain in Figure 1:
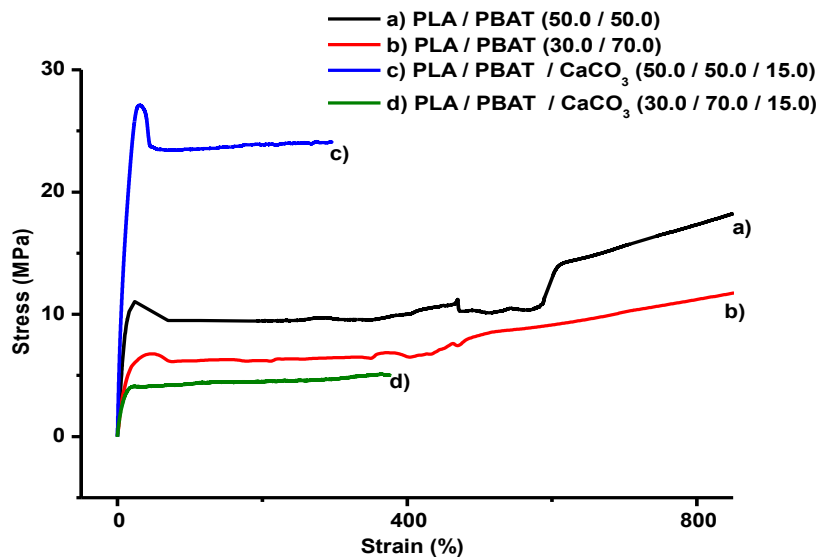
Figure 1.Diagram stress (MPa) x Strain (%) for PLA / PBAT blends and composites.

From Figure 1, stress value for PLA / PBAT (50.0 / 50.0) decreased from 11 MPa to 7 MPa for PLA / PBAT (30.0 / 70.0), in function of PBAT addition; strain values kept the same value about 820 %. The addition of 15% $CaCO_3$ in PLA / PBAT (50.0 / 50.0) increased from 11 MPa to 27 MPa stress value and reduced from 820 to 300 % strain value. Nevertheless, 15 % addition in PLA / PBAT (30.0 / 70.0) reduced both stress and strain: from 7 to 4 MPa and from 820 % to 400 %, respectively. In summary, a higher PBAT content in PLA/PBAT (50.0 / 50.0) was enough to prejudice reinforcement behavior intrinsic characteristic of bio-calcium carbonate previously obtained.

DSC is the recommended technique to reveal the variation in the thermal flow and to obtain the thermal critical points like melting point, enthalpy and specific heat. DSC analysis results and the degree of crystallinity reported as percent crystallinity for PLA / PBAT blends and its composites are listed in Table 3:

Table 3. DSC analysis results for PLA / PBAT blends and composites.

Blends and Composites	$T_c^{(a)}$ (ºC)	$\Delta H_{cc}^{(b)}$ (J.g^{-1})	$T_m^{(c)}$ (ºC)	$\Delta H_m^{(d)}$ (J.g^{-1})	$X_C^{(e)}$ (%)
PLA / PBAT (50.0 / 50.0)	71.7	7.2	86.9	21.1	29.9
PLA / PBAT (30.0 / 70.0)	62.1	9.8	88.3	10.7	3.4
PLA / PBAT / $CaCO_3$ (50.0 / 50.0 / 15.0)	69.7	7.1	87.4	12.0	10.8
PLA / PBAT / $CaCO_3$ (30.0 / 70.0 / 15.0)	87.9	8.6	86.7	8.8	1.0

(a) cold crystallization temperature; (b) crystallization enthalpy; (c) melting temperature; (d) melting enthalpy; (e) crystallinity.

As can be seen in Table 3, a higher addition of PBAT in PLA / PBAT blend contributed for increasing phase immiscibility in prejudice of blend morphology and crystallinity. The addition of 15 % of bio-calcium carbonate in PLA / PBAT (30.0 / 70.0) aggravated this behavior.

DSC thermograms for blends and composites were typical of partially crystalline materials, showing an endothermic peak, related to the melting (T_m) of the crystals, according it is shown in Figure 2:
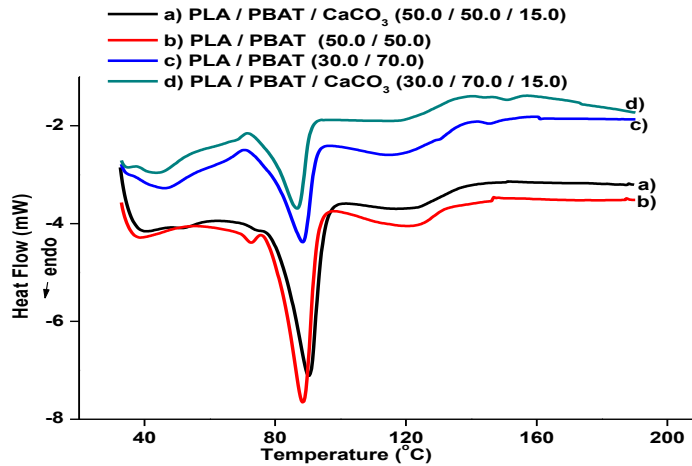
Figure 2. DSC thermograms of blends and composites.

Figure 2 shows that addition of 20% of PBAT in PLA / PBAT (50.0 / 50.0) blend reduced drastically enthalpy of fusion and contributed for a very low crystallinity. So, the incorporation of 15 % of calcium carbonate was significant and favorable in PLA / PBAT (50.0 / 50.0) blend and prejudicial in PLA / PBAT (30.0 / 70.0) blend.

In Table 4 is summarized thermogravimetric behavior for PLA/PBAT blends and composites:

Table 4. Thermogravimetric analyses results for PLA / PBAT blends and composites.

Blends and Composites	T_{onset} (°C)	T_{endset} (°C)	mass loss (%)
PBAT / PLA (50.0 / 50.0)	370.7	418.1	Negligible
PBAT / PLA (30.0 / 70.0)	382.0	415.0	Negligible
PLA / PBAT / CaCO$_3$ (50.0 / 50.0 / 15.0)	361.8	412.2	$\approx$ 15.0
PLA / PBAT / CaCO$_3$ (30.0 / 70.0 / 15.0)	361.0	410.0	$\approx$ 15.0

T_{onset}: initial degradation temperature; T_{endset} : final degradation temperature

As can be seen in Table 4, thermogravimetric analyses (TG), the addition of 15 % of bio-calcium carbonate in PLA / PBAT blends reduced about 20 °C the initial degradation temperature (T_{onset}); nevertheless, the final degradation temperature (T_{endset}) showed a non-significant difference. Mass loss was compatible with amounts involved in composites.

Morphologies of all blends and composite were examined by a scanning electron microscope Table-top Hitachi, 10 kV acceleration voltage, used to collected SEM images of sample. The samples were freeze-fractured in liquid nitrogen and coated with gold before analysis. In Figure 3 are shown micrographs related to PLA/PBAT blends and composites:
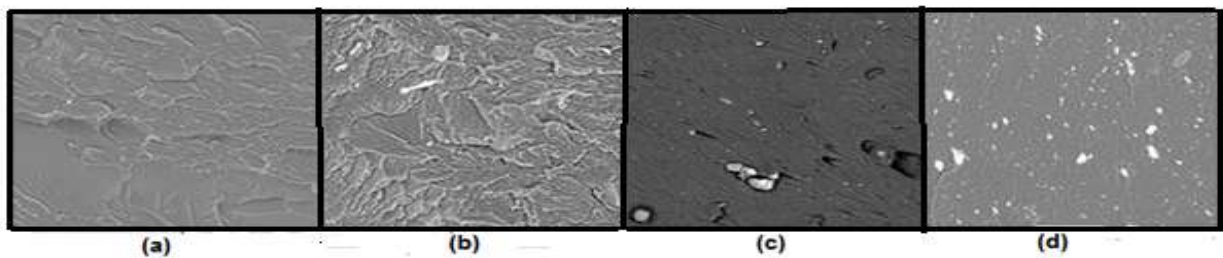

Figure 3. SEM micrographs of: (a) PLA / PBAT (30.0 / 70.0); (b) PLA / PBAT (50.0 / 50.0); (c) PLA / PBAT / CaCO$_3$ (30.0 / 70.0 / 15.0); (d) PLA / PBAT / CaCO$_3$ (50.0 / 50.0 / 15.0).

From Figure 3 it is observed that PLA shows an irregular dispersion and PBAT a continuous phase in blends; that is, PLA has a typical and irregular morphology *island-phase* [18] type and the PBAT a *sea – phase* type morphology, as can be observed in Figure 3, (a) and (b). White points in PLA / PBAT blends are due to non-dispersed bio-calcium carbonate, as shown in Figure 3, (c) and (d); nevertheless, bio-calcium carbonate contributed to a more homogeneous and smooth surface spite the agglomerates. All micrographs were enlarged 500 x.

Diffractograms presented in Figure 4 for PLA/PBAT blends and composites confirmed immiscibility phases described previously in DSC assessments:
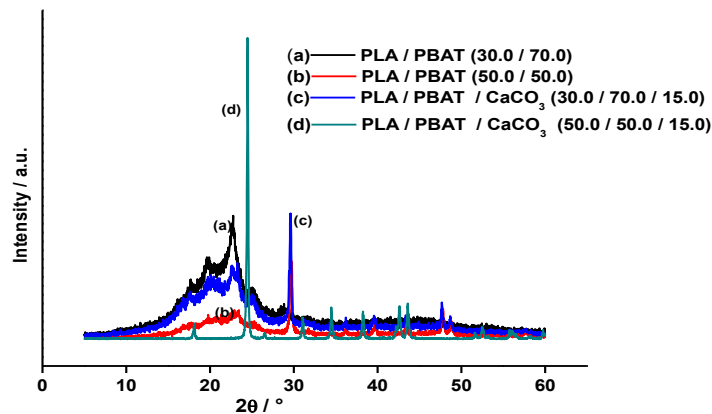

Fig. 4. XRD patterns of PLA/PBAT blends and its composites.

Figure 4 depicts that the large peak shown within 2 θ equal 17 ° and to 25 ° is typical of PLA / PBAT blends, with a higher intensity at 2 θ equal to 22 °. Several small diffraction peaks appeared in all samples and might be associated with PLA micro-crystallinity. Just 15 % of bio-$CaCO_3$ addition in PLA / PBAT (50.0 / 50.0) showed a well defined and high intensity peak at 2 θ, equal to 25 ° and characteristic of calcium carbonate.

4. CONCLUSIONS

Addition of bio-calcium carbonate showed effective for providing reinforcement of PLA / PBAT (50.0 / 50.0) blend from tensile tests. A higher amount of PBAT in PLA / PBAT blend prejudiced stress and morphology, due to a raise in phase immiscibility. Thermal behavior registered a reduction of approximately 20 ℃ for initial degradation temperature after insertion of 15 % of calcium carbonate in both PLA / PBAT blends; nevertheless, final degradation temperature for all samples investigated did not show significant differences. DSC investigations pointed toward a drastic reduction in crystallinity for PLA / PBAT (30.0 / 70.0), confirmed by DRX analyses.

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