

STUDY OF PBAT/PLA BIO-BASED FOAMS REINFORCED WITH CHICKEN EGG SHELL NANO POWDER COMPATIBILIZED WITH IONIZING RADIATION

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ABSTRACT

Eggshell is a solid waste, with production of several tons per day and it is mostly sent to landfills at a high management cost. It is economically viable to transform eggshell waste to acquire new values, transforming it into a bioplastic: a biodegradable polymer made from bio-mass. Chicken eggshell nano powder will be used for reinforcement of biodegradable polymers: PLA (polylactic acid) and PBAT (butylene adipate co-terephthalate), at 2.5, 5.0 and 10.0 %. Previous studies using PBAT/PLA, 50/50 blends containing 15% of chicken eggshell 125 μm improved mechanical behavior of net blends: values for both force and strain practically doubled, proving the effective reinforcement action of bio-calcium carbonate. Biodegradable polymers as PLA (polylactic acid) and PBAT (butylene adipate co-terephthalate) are thermoplastics which can be processed using conventional polymer processing methods. PLA is high in strength and modulus (63 MPa and 3.4 GPa, respectively) but brittle (strain at break 3.8%) while PBAT is flexible and tough (strain at break $\sim 710\%$). In order to reduce interfacial tension exhibited by PLA/PBAT blend, compatibilization is fundamental: herein it was used as compatibilizing agent PLA previously e-beam irradiated at 150 kGy: ionizing radiation induces compatibilization by free radicals, improving the dispersion and adhesion of blend phases, without the use of chemical additives and at room temperature. PBAT/PLA blends were prepared at the weight ratio of 82 / 18 together with compatibilizing agent: 5.0 % of PLA 150 kGy e-beam radiated. Samples were first homogenized in a co-rotating twin-screw extruder and further foamed in a mono-screw extruder, by using CO₂ as Physical Blowing Agent (PBA). Characterizations involved: DSC, TGA, FTIR, XRD, Tensile Strength and Elongation at Break.

1. INTRODUCTION

Eco-efficient plastics: natural polymers, biopolymers and synthetic polymers based on renewable resources are the basis for the twenty-first century portfolio of sustainable and efficient plastics. The interest on these polymers is considerable, due to a decrease of world resources in oil; in addition, the lack of safe disposal and efficient degradation methods of synthetic polymers are posing an ecological threat to vegetation and animals [1]. A large amount of plastic waste is being generated rapidly all over the world, being the origin of eight complex problems in aquatic environment: plastic debris pollutes, plastic entangles marine life, consumption of plastic items by marine fauna, petroleum-based plastic polymers biodegradation is time-consuming, broken plastic and its pellets interrupt the food web, interfere the sediment populations, oceanic litter destroying the primary habitat of new emerging life and marine plastic litter

r also causes a major damage to vessels [2]. As alternative to synthetic plastics, biodegradable polymers are a newly emerging field [1 – 15].

Biodegradable polymers offer a great variety of advantages to environmental conservation and can be classified into two major categories: natural polymers and synthetic polymers. Polymers obtained basically from renewable sources reduce the environmental impact in order to achieve certain technical requirements and are fully biodegradable. Natural polymer based materials offer a feasible alternative to the traditional polymeric materials when recycling of synthetic polymer is not cost effective or technically impossible.

PBAT (Poly(butylene adipate-co-terephthalate)) is an aliphatic-aromatic random co-polyester, fully biodegradable, prepared from 1,4 – butanediol, adipic acid and terephthalic acid: a synthetic polymer based on fossil resources, 100% biodegradable, with high elongation at break. [16]. PBAT can be used in several applications, such as packaging materials, hygiene products, biomedical fields, industrial composting, among others [17 – 21]; nevertheless, PBAT has poor thermal and mechanical properties, that can be overcome with addition of fillers.

Poly(lactide) or poly(lactic acid) (PLA) is a linear, aliphatic thermoplastic polyester, used for different applications ranging from medical to packaging, resorbable and biodegradable under industrial composting conditions [22]; its rheological properties, especially its shear viscosity, have important effects on thermal processes. Some properties of PLA such as inherent brittleness, low toughness, slow crystallization, poor melt strength, narrow processing window and low thermal stability and high cost limit their large scale-applications [23 - 25].

PLA and PBAT binary blends exhibited improved properties, when compared to pure PLA. The addition of filler to PLA/PBAT blends acted as reinforcement, in terms of mechanical strength behavior.

In this paper was used bio-calcium carbonate from avian egg shells, as blends reinforcement. Daily, tons of chicken eggshells are discarded, generating commercially devalued waste from restaurants, food industry and homes. Currently, egg production throughout the world is 65.5 million metric tons per year [26]. The eggshell is rich in calcium carbonate, natural bio-ceramic composite with a 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 that can be efficiently used for polymer composites [27].

Unfortunately, PLA/PBAT blends filled with calcium carbonate (CaCO_3) present poor mechanical properties due to a poor interfacial adhesion, considering different glass transition exhibited for PLA (56 °C) and PBAT (-34 °C). In order to cope with this problem, irradiation was used to improve the compatibility between immiscible polymers in a blend. Irradiation leads to changes not only in the interphase but also in the bulk of both polymers (chain scission, crosslinking, etc.). Herein it was used as compatibilizing agent PLA previously e-beam-radiated at 150 kGy, air environment, $10.5 \text{ kGy}\cdot\text{h}^{-1}$. Güven and collaborators have proposed the use of ionizing radiation in replacing chemical compatibilizing agents for thermoplastic materials with enhanced properties [28-36].

Foam technology has been developing since 1930, using blowing agents in polymer processing. Polymer foams consist of two phases: a polymeric matrix and entrapped, well

dispersed cells generated by blowing agents. Foams have several advantages: low density, insulating capability, energy absorption, *etc.* These make foams a desired product in many applications such as packaging, floating materials, paddings, shields for reducing noise, shoes, *etc.* In addition, cells in the foams accelerate the degradation, since they facilitate the infiltration of water toward the interior of the polymer and triggered the degradation process by hydrolysis [37].

Carbon dioxide was used as Physical Blowing Agent (PBA): it has a regular solubility and is considered as an eco-friendly gas. A PBA is capable to produce a cellular structure via foaming process and it is typically applied when blown material is in liquid stage. Cellular structure in a matrix reduces density, increasing thermal and acoustic insulation [38 - 39].

The proposal of present work is the development of bio-based foams from PBAT/PLA 82/18 blend, reinforced with chicken eggshell nano powder compatibilized with PLA ebeam-radiated at 150 kGy and further assessed for DSC, TGA, FTIR, XRD, Mechanical Essays and Soil Burial Test.

2. MATERIALS AND METHODS

2.1. Materials

PLA and PBAT polymers, with main characteristics described in Table 1:

Table 1. Main characteristics of used polymers

Characteristics of PLA	Characteristics of PBAT
Grade: Ingeo Biopolymer 3251 D	Commercial name: Ecoflex FS
Supplier: Nature Works	Supplier: BASF
Melting Point : 168 °C	Melting Point: 110 – 120 °C
Glass transition temperature: 62 °C	Glass transition temperature: -30°C
Average molecular weight: 100,000 g.mol ⁻¹	Average molecular weight: 40,000 g.mol ⁻¹

Both PLA and PBAT were dried at 70°C for 12 hours before processing.

PLA e-beam radiated at 150 kGy: compatibilizing agent, from PLA e-beam radiated at 150 kGy, dose ratio 10.00 kGy/s, Dynamitron II electrons accelerator, 1.5 MeV energy, 25 mA current, 37.5 kw power, in CTR-IPEN/CNEN-SP.

CaCO₃ (calcium carbonate) from avian eggshells: white chicken eggshells were subjected to a thorough cleaning using tap water for removing of internal membranes. Afterwards, clean eggshells were kept for 4 hours in a 100 °C water bath and finally dried at 100 ± 2°C for 2 h in an air-circulating oven. Eggshells were size reduced to fine powder, particle size equal to 38 µm, by using ball mills and granulometric sieve, respectively.

38 µm bio calcium carbonate was subjected to a sonochemical process, via a high intensity ultrasonic cell disruptor, 20 kHz and 500 W/cm². Resulting powder was dried at 100 ± 2 °C, for 24 h, in order to reduce its moisture content to less than 2 %; scanning electron

microscopy accomplished in a FEG equipment model F-50 in the powder previously gold coated in a Balzers SCD 050 sputtering system presented the micrograph shown in Figure 1:

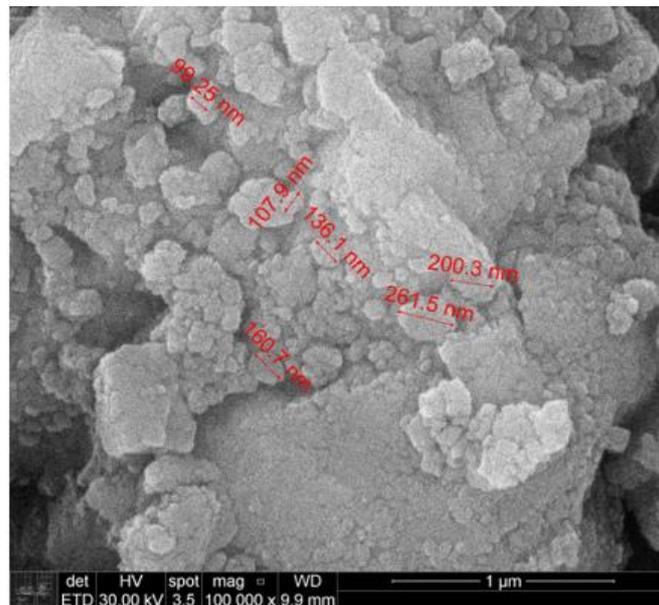


Figure 1. chicken eggshell nano powder

CO₂ (Carbon dioxide): physical blowing agent (PBA), selected according to good diffusion in PLA foaming [40].

2.1.1 Preparation and processing

Composite materials were prepared according to Table 2; they were first homogenized by melting extrusion process, using a co-rotating twin-screw extruder (HAAKE Rheomex 332p, 3.1 L/D, 19/33 compression ratio), by using a 120 to 145°C temperature profile and 50 rpm.

Table 2: Material designation and composition for PBAT/PLA/CaCO₃/PLA 150 kGy e-beam radiated

Designation	PBAT (wt%)	PLA (wt%)	Bio CaCO ₃ nanopwder (wt%)	PLA 150 kGy, e-beam (wt%)
PBAT	100	--	--	--
PBAT82	82	18	--	--
Sample 1	82	18	2.5	5
Sample 2	82	18	5.0	5
Sample 3	82	18	10.0	5
PLA	--	100	--	--

Homogenized samples (pellets) were further subjected to extrusion under pressure, by expansion physical method using carbon dioxide (CO₂) as blowing agent , at 10 bar

(approximately 10 kgf.cm^{-2}). It was used a mono-screw specific for foaming, maintaining the same temperature profile: $130 \text{ }^\circ\text{C}$ to $145 \text{ }^\circ\text{C}$.

3. Characterization

3.1 Differential Scanning Calorimetric Analyses (DSC)

Thermal behavior was examined in a DSC-50 Shimadzu apparatus, according to ASTM D3418-08. Heating was carried out from $30 \text{ }^\circ\text{C}$ to $270 \text{ }^\circ\text{C}$, nitrogen atmosphere, N_2 flow rate = 50 ml/min and temperature rate = $30 \text{ }^\circ\text{C/min}$.

3.2 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). TGA were performed using two apparatus: a TGA Shimadzu, model 51 and a TGA Mettler Toledo, according to ASTM E1641-07, by using $10 - 20 \text{ mg}$ of sample, within a 25 to 600°C program, at a $20^\circ\text{C.min}^{-1}$, in a nitrogen flow of 50ml.min^{-1} .

3.3 ATR-FTIR (Attenuated Total Reflection Fourier Transform Infrared Spectroscopy)

FTIR is a sensible method for identifying chemical modification in a material, and so, is capable to detect chemical modifications in a polymeric material. This method detects vibrational movements imparted from chemical bonds for the material that is being analyzed. As each chemical group absorbs vibrational energy at a given value, it is possible to differentiate them via infrared spectrum. Spectra were obtained from a Perkin-Elmer, Universal ATR Sampling Accessory –Spectrum 100 FT – IR Spectrometer. Setup collection sample was adjusted for 64 scans, within a $4,000$ to 650 cm^{-1} range.

3.4 XRD (X-Ray Diffraction Analysis)

X-rays diffraction is a technique used for determining anatomic structure: it consists in a constructive interference of a wave from X-rays incident beam in relation to an uniform atomic spacing.

In this technique it is applied Bragg's Law, defined by $n\lambda = 2d\sin\theta$, where $n\lambda$ is an entire value for wavelength generated by an specific target according to a give electronic transition and $\sin\theta$ is the angle where it occurs the constructive interference; therefore, it is possible to determinate interplanar distances (d) for each crystalline plane. The identification of crystalline phase of a material is given from a database defined by JCPDS (Joint Committee on Powder Diffraction Standards) that compares position of obtained peaks with intensity relationship.

It was used herein a X-Ray diffractometer, Rigaku Multiflex, graphite monochromator, 40 kV , 20 mA , X-rays tube, copper anode $\lambda_{Cu_{k\alpha}} = 1,5418\text{\AA}$, scanning 2θ within 3° to 60° , speed $0.06^\circ/4$ seconds, fixed time. It provides, among other, information on samples crystallinity, via diffractograms, distinguishing between amorphous and crystalline state.

3.5 Tensile and Elongation at Break

Tensile and elongation at break essay is a relevant instrument for evaluating loss of properties and evolution of degradative process of the polymer. Parameters that contribute for mechanical behavior of polymers are: chemical structure, crystallinity degree, molar mass, moisture, reinforcing agent present, among others. All these properties are modified during degradation processes. In case of reinforcing agents, the concentration is not changed; nevertheless, their interaction can be modified in consequence of chemical modifications suffered by the polymer. Tensile and elongation at break tests were accomplished at $25 \pm 5^\circ\text{C}$, in an EMIC model DL 300 universal essay machine, 20 kN load cell, $50 \text{ mm}\cdot\text{min}^{-1}$, in accordance with ASTM D 638-14. Specimens were conditioned at $25 \pm 5^\circ\text{C}$ and $50 \pm 5\%$ relative humidity, for 24 hours, prior test.

3.6 Scanning Electron Microscopy (SEM)

4. RESULTS AND DISCUSSION

4.1 Differential Scanning Calorimetric Analyses (DSC)

DSC heating curves for analyzed materials shown in Table 2 are shown in Figures 1 and 2:

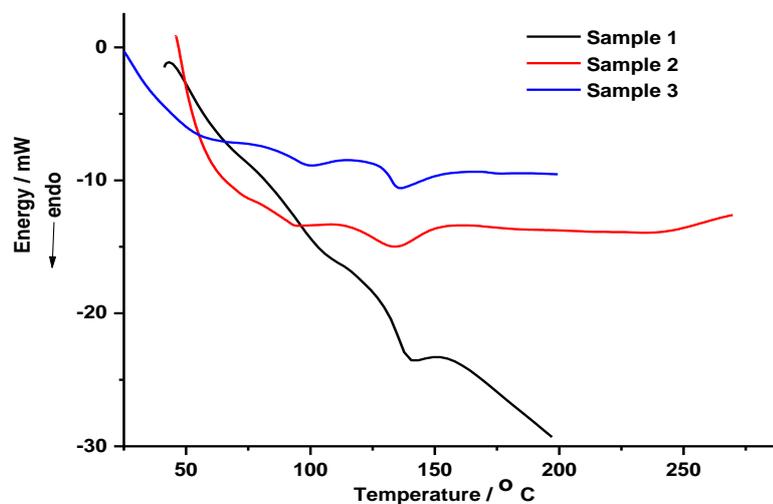


Figure 1: Melting curves for analyzed samples

Sample 1, containing lesser amounts of bio-nano powder, presented a different behavior when compared to samples 2 and 3.

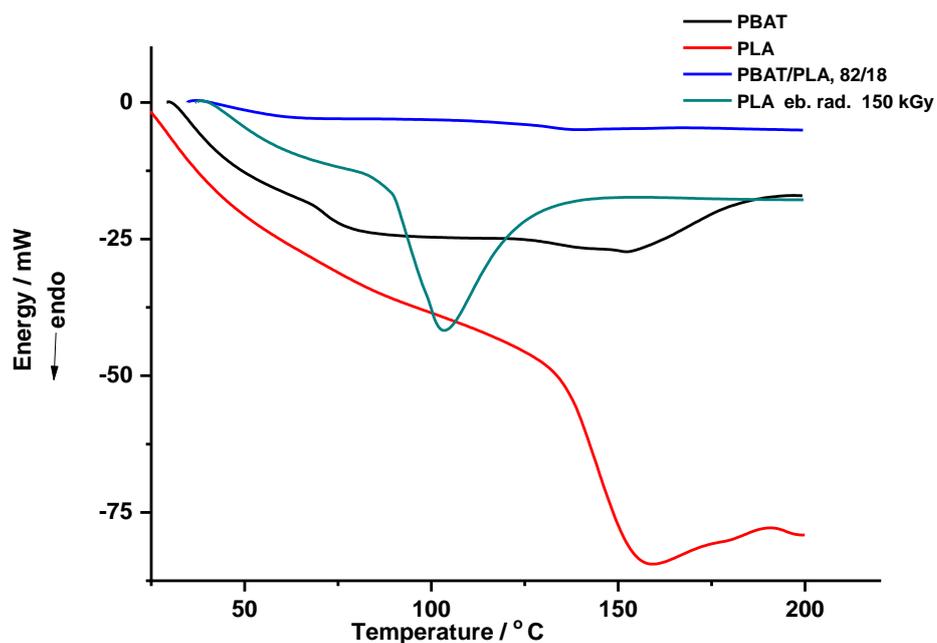


Figure 2. Melting curves for samples constituents

DSC curves found for samples constituents were expected, according to literature values.

In Table 2 are listed thermal characteristics for samples and their constituents:

Table 2. Thermal Characteristics for samples and constituents:

	PEAK (° C)	ONSET (° C)	ENDSET (° C)	Fusion Enthalpy (j.g ⁻¹)
PLA	146.55	134.86	168.30	19.15
PBAT	160.83	155.62	167.37	3.08
PBAT82	138.80	130.84	156.29	1.92
PLA 150 kGy, eb	99.84	89.81	117.13	1.09
Sample 1	140.52	169.55	123.00	12.22
Sample 2	152.39	159.17	168.68	5.21
Sample 3	135.99	127.62	152.72	4.862

Onset temperature for samples increased in function of nano powder incorporation.

4.2 Thermogravimetric analyses (TG)

TG was carried out to investigate the effect of processing on the thermal decomposition of PLA and PBAT under nitrogen atmosphere, as can be seen in Figures 3 and 4:

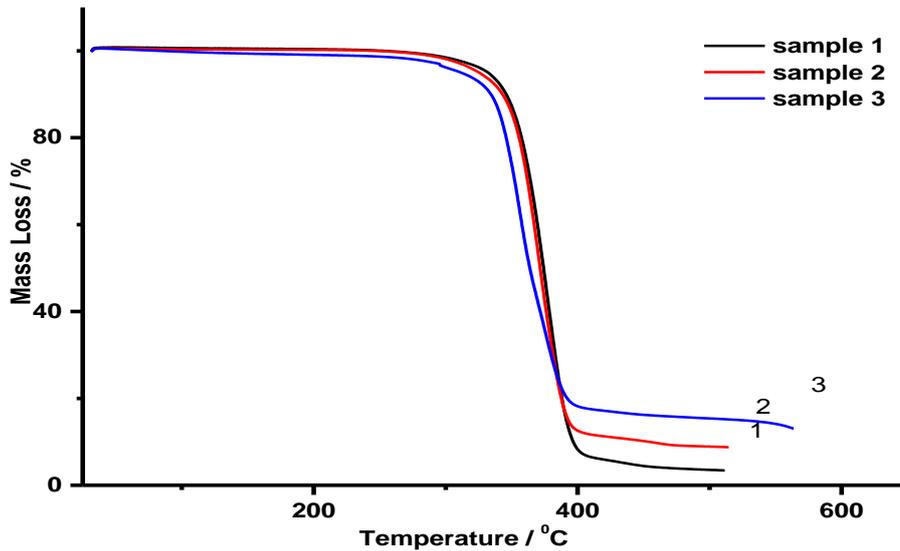


Figure 3. TG curves for samples

Sample 1, containing lesser amounts of bio-nano powder, presented a more stable behavior when compared to samples 2 and 3.

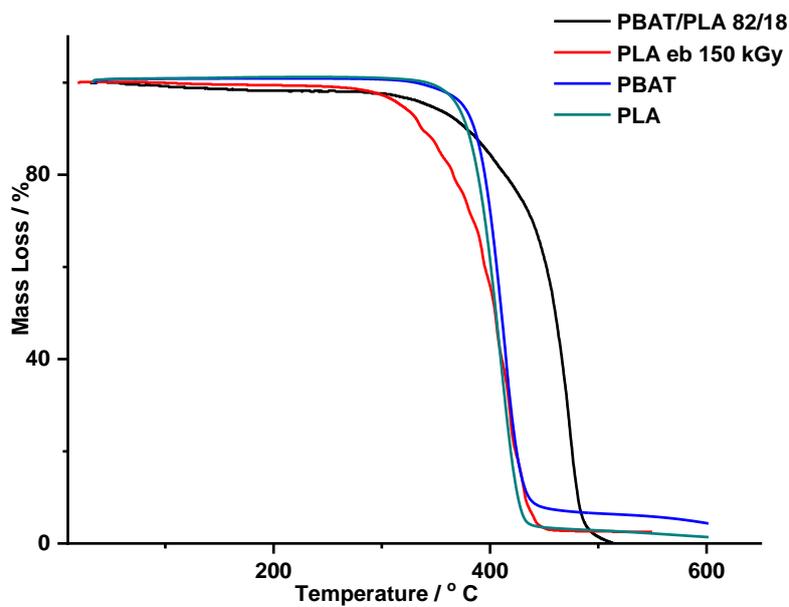


Figure 4. TG curves for constituents.

TG curves found for samples constituents were expected, according to literature values.

In Table 3 are listed thermal characteristics for samples and their constituents:

	ONSET (° C)	ENDSET (° C)	Weight Loss (%)
PLA	358.89	521.50	89.33
PBAT	356.14	496.92	91.39
PBAT82	308.47	440.47	87.67
PLA 150 kGy, eb	271.15	466.02	95.91
Sample 1	408.68	588.88	95.13
Sample 2	405.23	519.58	90.20
Sample 3	383.35	530.51	86.42

The onset for mass loss often defines the upper limit of thermal stability for the material.

4.3 ATR-FTIR (Attenuated Total Reflection Fourier Transform Infrared Spectroscopy)

FRI spectra for samples and their constituents are shown in Figures 5 and 6:

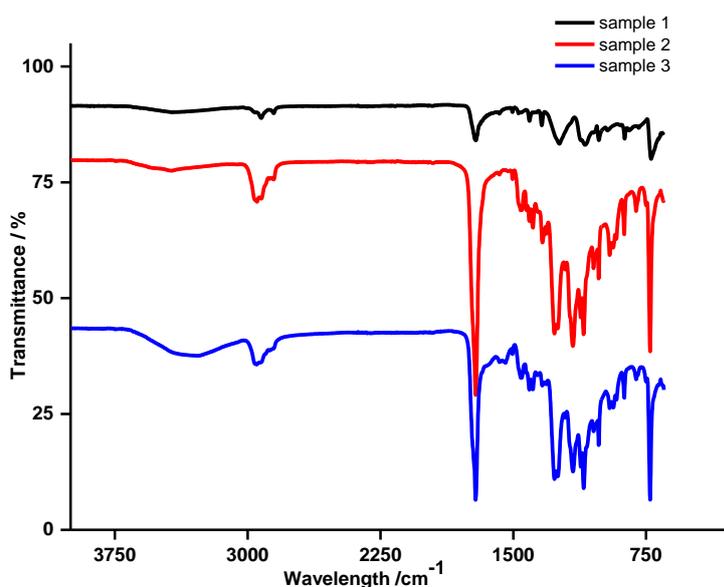


Figure 5. FTIR of samples 1, 2 and 3.

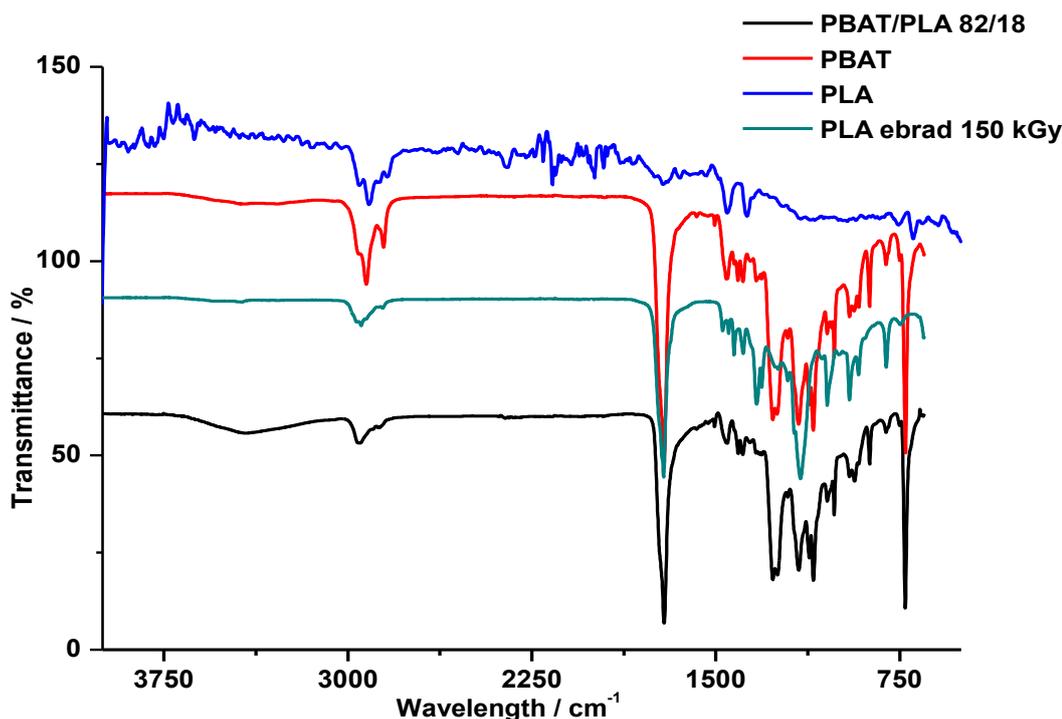


Fig.6. FTIR of constituents samples

For PLA, the peak at around 752 cm^{-1} associated with the rocking vibration of α -methyl; peak at around 864 cm^{-1} associated with the ester (O-CH-CH₃); the peak at around 1042 cm^{-1} , 1080 cm^{-1} and 1180 cm^{-1} associated with the stretching vibration of C-O-C; the peak at 1381 cm^{-1} associated with the CH symmetric bending vibration; the peak at around 1450 cm^{-1} associated with the CH₃ antisymmetric; the peak at 1748 cm^{-1} associated with the carbonyl C=O stretching vibration; and the symmetric and antisymmetric stretching vibration of CH₃ of saturated hydrocarbons were found at 2943 cm^{-1} and 2997 cm^{-1} , respectively [47 - 48].

For PBAT, the peak at 725 cm^{-1} associated with the bending vibration of CH-plane of benzene ring; the symmetric stretching vibration of trans-C-O was found at 937 cm^{-1} ; the peak at 1018 cm^{-1} associated with the bending vibration at the surface of adjacent hydrogen atoms on the phenyl ring; the peak at 1103 cm^{-1} associated with the left-right symmetric stretching vibration of C-O; the peak at 1265 cm^{-1} associated with the C-O symmetric stretching vibration; the peak at 1408 cm^{-1} associated with the trans-CH₂-plane bending vibration; the peak at 1504 cm^{-1} associated with the skeleton vibration of the benzene ring; the peak at 1713 cm^{-1} associated with the C-O stretching vibration; and the peak at 2959 cm^{-1} associated with the CH₂ asymmetric stretching vibration [47 - 48].

Absorption spectral of PLA/PBAT blends showed the up-shift of CH-plane of the benzene ring vibration from 725 to 729 cm^{-1} . Ester vibration peak in PLA shifted from 864 to 872 cm^{-1} [49]. There was however no clear evidence of interaction between PLA and PBAT in the blends

Absorption spectra for samples were similar to shown by their constituents, according to amounts involved.

4.4 XRD (X-Ray Diffraction Analysis)

X-ray diffraction patterns of samples and their constituents are shown in Figures 7 and 8:

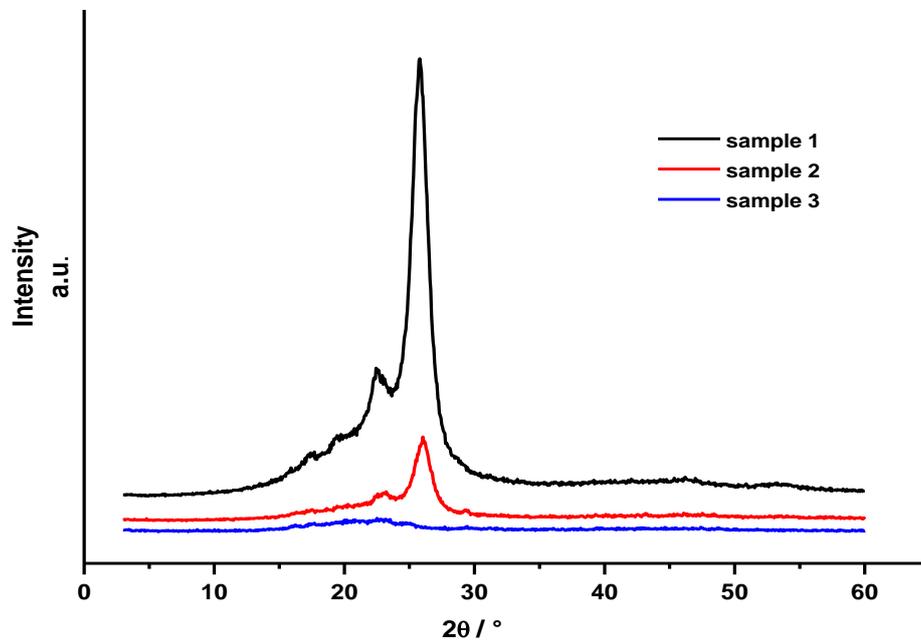


Fig. 7. DRX diffractograms for samples

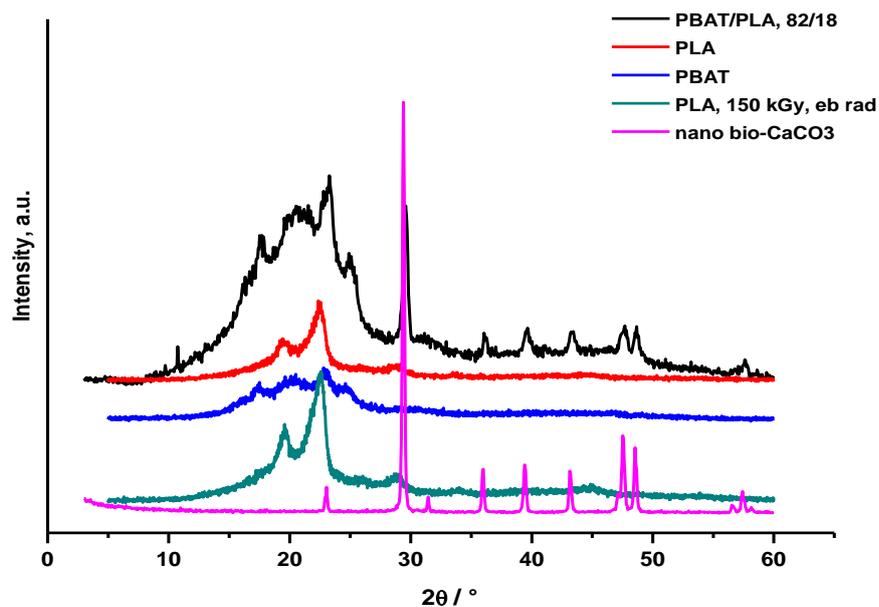


Fig. 8. DRX diffractograms for samples constituents

In general, the sample is composed by crystals and amorphous phases: the sharp peaks are related to crystallites diffraction and larger peaks are related to amorphous phases. In Figure 8, pure PBAT and PLA exhibited four peaks in 17.5°, 20.5°, 22.5° and 24.5°, in which 22.5° 2θ was the most intense. Nano-CaCO₃ exhibited the most intense peak at 30.0 2θ, among other crystalline ones. PLA e-beam radiated at 150 kGy exhibited two peaks at 20.0 and 22.0, 2θ, proving the efficacy of e-beam radiation treatment.

In Figure 7 is notorious that there was a better interaction between sample 1, which contains a lower chicken eggshell nano powder when compared to samples 2 and 3; probably, this is due to a low efficacy of compatibilizing PLA 150 kGy, e-beam radiated.

4.5 Tensile Strength and Elongation at Break

Tensile Strength and Elongation at Break for samples and their constituents are presented, respectively, in Figures 9 and 10:

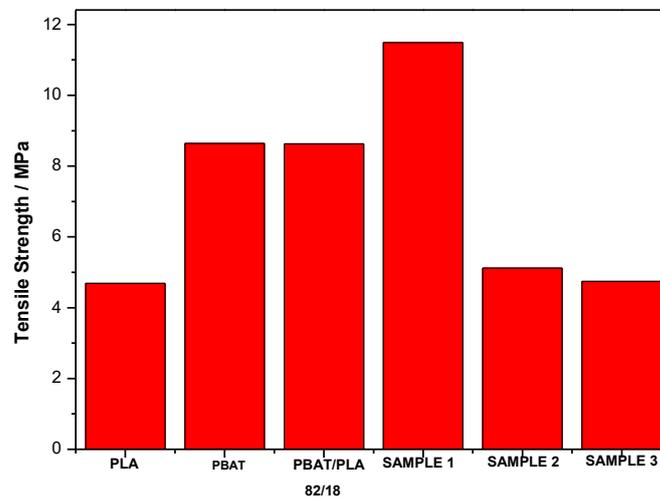


Figure 9. Tensile Strength for samples and their constituents

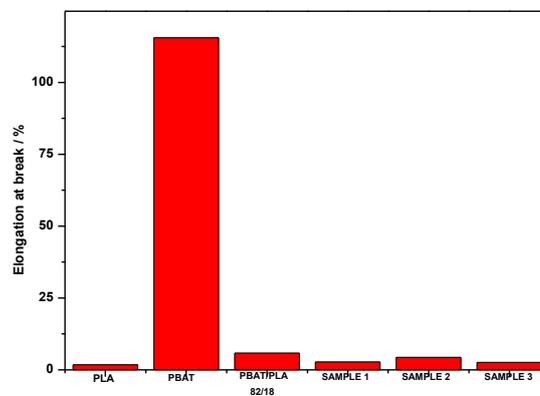


Figure 10. Elongation at break for samples and their constituents.

In Figure 9 it can be seen that PBAT/PLA 82/18 and PBAT exhibited the same high value for tensile strength: 8 MPa. Sample 1, containing lower nano bio-CaCO₃ (2.5 %), showed a higher value: 11 MPa, pointing toward an effective PBAT and PLA blend interaction under influence of PLA 150 kGy e-beam used as compatibilizing agent. Nevertheless, compatibilizing agent showed ineffective for higher nano-bio CaCO₃ contents: 5.0 and 10.0 %, respectively.

In Figure 10, it is evident that just PBAT, as expected, showed a higher flexibility and consequently, a high elongation at break.

5. CONCLUSIONS

DSC analyses for sample 1, containing a lower amount of nano bio-CaCO₃ (2.5 %) - presented a higher value for fusion enthalpy, when compared to samples 2 and 3: 5.0 % and 10.0 %, respectively). Either for TGA investigations, sample 1 presented a better behavior, considering its initial thermal degradation (onset). Absorption spectra for sample 1, via DRX diffractograms, showed clearly a better interaction between sample 1 and its constituents, when compared to samples 2 and 3; probably, this was due to a low efficacy of compatibilizing PLA 150 kGy, e-beam radiated, for samples containing a higher amount of reinforcing agent (nano bio CaCO₃). Results from FTIR and DSC measurements suggested that PLA and PBAT were immiscible. Tensile strength corroborated an effective interaction among constituents, according to high result obtained for sample 1: 11 MPa. As expected, elongation at break results were very low for all evaluated specimens, except for PBAT: higher than 100 %. In summary, and according to accomplished investigations, PBAT/PLA 82/18 blends, compatibilized with 5% of PLA 150 kGy e-beam radiated, will be capable to provide bio-based foams, ratifying previous studies.

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