Study of the effect of Dicumyl Peroxide on morphological and physical properties of foam injection molded Poly (lactic acid) / Poly (butylene succinate) blends.

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Abstract

Blends of Poly (lactic acid) (PLA) with Poly (butylene succinate) (PBS) were compounded in presence of dicumyl peroxide (DCP) for compatibilization and foaming capability improvement. A PLA/PBS blend with a weight ratio of 40/60 was prepared with contents of DCP of 0%, 0.1%, 0.4% and 1% by weight. The neat PLA and PBS, and blends were foam injection molded using azodicarbonamide as chemical foaming agent. The thermal and rheological behaviors of the materials and blends are discussed. After chemical foaming, the mechanical response of the obtained samples is compared and the morphology of the obtained foamed structures is analyzed and discussed. The best mechanical properties and foaming capabilities were obtained with 0.1%wt of peroxide, obtaining impact strength values similar to neat-foamed PBS and cell population densities higher than neat PLA. Peroxide contents higher than 0.4 %wt tend to decrease foaming capabilities and mechanical properties of the blends due to excessive crosslinking.

Keywords

Foam injection molding, biopolymer, PLA/PBS blends, compatibilizer, crosslinker, DCP

1. Introduction

In recent years, there is a global concern about the consumption, use and disposal of non-biodegradable materials, including plastics, due to the adverse effects on the environment. The decomposing time of regular polymers in the environment is usually too long, so they tend to accumulate in landfills and natural habitats, contaminating and threatening the different life forms of the affected places [1]. Furthermore, the awareness of fossil fuel consumption is critical to encourage the search for new ways of producing or replacing currently used materials and products [2]. Hereby, biodegradable polymers have made their way as an alternative to the use of regular polymers in general-purpose applications. However, their relatively high cost and different mechanical properties compared to certain commodity polymers, are limitations for their broad use in some applications [3].

Two of the most commonly used biodegradable polymers in the industry are poly (lactic acid) (PLA) and poly (butylene succinate) (PBS). PLA is a compostable thermoplastic polyester obtained from renewable resources such as cornstarch and sugarcane [2]. It has been one of the most widely used and studied biopolymers because of its properties-cost ratio [4]. On the other hand, PBS is a synthetic biodegradable aliphatic polyester obtained from the polycondensation of 1,4-butanediol with succinic acid [2]. This material has attracted considerable attention because of its high flexibility, impact strength, thermal and chemical resistance as well as good processability. Yet, this material is still too expensive compared with other polymers and it has low stiffness, which limit its use to high added value applications [5]. However, the high cost is due to the low worldwide production capacity, which is a variable that may improve over time [6].

With the increasing global consumption, particularly of plastics, the use of polymer foams has become an alternative of great interest. A foamed material allows reducing the weight of plastic products enhancing its cost-benefit ratio. Foaming also tends to increase some properties an characteristics like impact strength and the thermal and acoustic insulation [7]. However, the reduction of other properties such as rigidity and resistance should be considered in the final application [8].

PLA foams have been analyzed as potential replacement for expanded polystyrene (EPS)[9]. However, PLA has some limitations such as its low melt strength, low toughness, low deflection temperature and high brittleness [10]. On the other hand, the implementation of PBS in the foam industry is limited due to its low molecular weight as well as its low melt strength and viscosity, which both reduce the foaming capabilities

[11]. To overcome these limitations, this work proposes a material blend, in combination with the use of crosslinking agents as approaches that could improve these materials foaming capabilities.

PLA/PBS blends have been widely studied due to their complementary characteristics, like low price and high stiffness of PLA contrasted with high toughness of PBS as reviewed by Nofar et al. [4]. In 2015, Deng Y et al [5] studied the effects of PBS content from 0 to 90% on PLA/PBS blends on thermo-mechanical properties through phase morphology analysis. They found that the Young's modulus and the tensile strength decrease as the concentration of PBS is increased. They disclosed the phase separation between both materials suggesting that the incorporation of a compatibilizer is required to improve the interfacial adhesion and miscibility of both phases. Although PLA/PBS miscibility has not yet been entirely cleared up, several research works have attempted to improve the materials compatibility trough the incorporation of compatibilizers [12].

Dicumyl peroxide (DCP) has been used as an in situ compatibilizer and chain extender (CE) for biopolymers. As reviewed by Muthuraj et al. [3], DCP is an initiator to form crosslinked or branched structures by heterogeneous and homogeneous radical coupling reactions between both PLA and PBS polymers, producing small sized inclusion phases and a good interfacial adhesion between the blend components. Ji et al. [13] reported a tensile strength decrease although with a significant increase of elongation at break in PLA/PBS blends when 0.2 and 0.3 %wt of peroxide were used. Wang et al. [14] also reported that the addition of DCP led to a reduction on the domain size of PBS phases as well as better interfacial adhesion between PLA and PBS when 0.1 %wt of peroxide was added in blends with 20 %wt PBS. The impact strength was also significantly increased. Ji et al. [13] reported that in blends with 20 %wt PBS, the addition of 0.3 %wt DCP increased the elongation at break from 49% to 205% and the tensile strength from 55 to 80 MPa.

Chain extenders (CE) have also been used to improve PLA and PBS foaming capabilities. Ludwiczak et al. [15] used the epoxide-based chain extender *Joncryl* in contents from 0.2 to 1.5%wt for the chemical foaming of PLA. In the study, a fine cellular structure was obtained with a low density (0.7 g/cm^3). When 1.5 %wt of CE and 1 % CFA were used, the CE significantly influenced the cell structure by increasing the amount of small cells. Bocz et al.[16] also used *Joncryl* to analyze the foaming of natural fiber reinforced PLA prepared by supercritical CO_2 assisted extrusion. They found that the combined application of chain extender and talc effectively promoted the formation of uniform cell structures.

Gottermann et al.[17] studied the effect of different chemical modifiers like *Joncryl*, DCP, styrene maleic anhydride, among others, on the thermal and rheological properties of PLA for extrusion foaming. They found that the best modifier to enhance melt crystallization rate and melt strength was DCP. Tobias Standau et al.[18], investigated the effect of DCP on the rheological properties and its effect on the expansion behavior and foam properties of PLA extruded foams. They found that modified PLA foam compared to neat PLA foam reached twice the compression strength with a reduction of 30% in its density when 0.2% wt of peroxide was used. Furthermore, the effect of DCP on the morphological and physical properties of PBS foams was analyzed by Boonprasertpoh et al. [11] and Feng et al. [19]. Both works evidence increases on the material viscosity, melt strength, and mechanical properties such as tensile strength when DCP was used.

The objective of this paper is to analyze for the first time the effect of DCP on foam injection molded PLA/PBS blends with chemical foaming agents (CFA) in order to overcome the limitations of the neat materials. In this work, the mechanical and morphological properties of PLA/PBS/DCP blends are investigated to have a better understanding of how the presence of DCP affect the foaming capabilities and performance of the modified blends.

2. Experimental setup

For the analysis, neat PLA and PBS were preconditioned for compounding in a twin-screw extruder both with and without compatibilizer. Then, the obtained blends and new neat materials were again preconditioned under the same conditions. They were dry-mixed with a chemical foaming agent for foam injection molding in order to analyze the foaming capabilities and properties of each materials. Finally, test samples were cut and characterized. Processing conditions for compounding and injection foaming were fixed in order to avoid possible changes in blends properties and performance related to processing parameters. Below, all the materials, equipment and processes used are presented.

2.1. *Materials*

For the experimental setup, two biopolymers, one peroxide and one chemical blowing agent were used. PLA 4043D was obtained from Nature Works LLC., USA, with a melt-flow index of 6.15 g/10 min (at 210°C and 2.16 Kg) and a solid density of 1.24 g/cm^3. PBS FZ91 was acquired from PTT MCC Biochem Co., Ltd., Thailand, with a melt-flow index of 9.46 g/10 min (at 190°C and 2.16 Kg) and a solid density of 1.26 g/cm^3. A commercial Dicumyl peroxide (DCP) with 98 %wt purity was used as compatibilizer and crosslinker in the blends.

An exothermic chemical foaming agent (CFA) was provided by Arcolor S.A, Arcoplast PE 2589 master batch with a 25%wt content of azodicarbonamide in a carrier of PE. The CFA has a processing temperature of 210°C. This agent was selected because it has been previously tested by other researchers in other biopolymer formulations [11], [20]. CFA with biodegradable carrier are not commercially available. Therefore, CFA masterbatches with PE carriers were used. However, the low CFA contents required for foaming do not compromise the biodegrability, processability and performance of the blend.

2.2. *Compound Preparation*

PLA and PBS were dried in a vacuum oven Vacutherm VT 6130 from Heraeus Instruments. A temperature of 80°C and vacuum pressure of 200 mBar for 8 hours were used in order to avoid hydrolysis degradation during processing.

The PLA/PBS %wt ratio was set at 40/60 with fixed DCP contents of 0 wt %, 0.1 wt %, 0.4 wt % and 1 wt %. This ratios and contents were defined as result from previous works performed at the ICIPC with PLA/PBS/DCP blends analysis for other applications and as a conclusion from results disclosed in the literature, where higher PBS contents in the blends showed better mechanical and rheological properties. Regarding the DCP content, best results reported in the literature are usually obtained in the range of 0.1 to 1 %wt. Table 1 summarizes the blend code names and compositions.

Table 1 Blends compositions

Blend	%PLA	%PBS	%DCP
PLA	100	0	0
PBS	0	100	0
0DCP	40	60	0
0.1DCP	40	60	0.1
0.4DCP	40	60	0.4
1DCP	40	60	1

For the compounding process, a twin-screw extruder Micro 27 from Leistritz with 27 mm screw diameter, 44 L/D and sequential feeding. The screw and extruder configurations are presented in Figure 1.

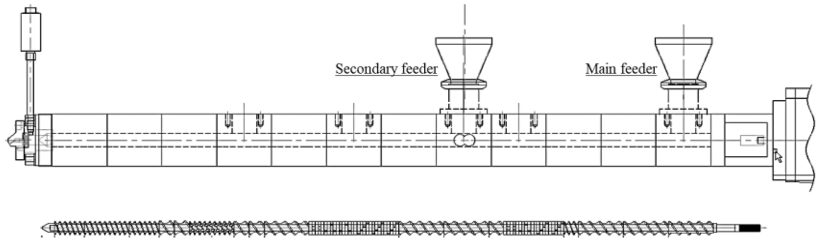

Figure 1 screw and extruder configuration

The extrusion process parameters were set as follows: screw speed of 110 rpm, an increasing temperature profile from 170°C at the feeding zone to 200°C at the die with a flow rate of 5 kg/h. As presented in Figure 1, two feeders were used. The main feeder was used for the PLA/PBS blends and the secondary feeder was used for the DCP powder in order to integrate the peroxide with the premixed melt.

2.3. *Samples foaming*

Test samples were injection molded on a conventional injection molding machine Arburg Allrounder 420CG of Φ35mm screw diameter and 100 kN clamping force, with a two disk-shaped mold of 6 mm of thickness and a diameter of Φ85 mm; all as presented in Figure 2. For sample preparation, the pelletized blends were dried under the same conditions mentioned earlier and then they were dry-mixed with CFA at 3 %wt before the injection molding process.

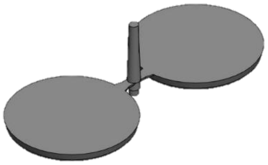

Figure 2 Injection molded discs

The injection process parameters were set for foamed samples as presented in Table 2.

Table 2 injection molding process parameters

	Foamed samples
Melt temperature [°C]	210
Shot volume [Cm3]	60
Injection flow rate [Cm3/s]	38
Packing pressure [Bar]	--
Packing time [s]	--
Cooling time [s]	100
wall temperature [°C]	40

The same shot volume was defined for all samples. The cavity was partially filled during the injection phase and no packing pressure was applied to allow part foaming inside the cavity. The cooling time was adjusted long enough to avoid part swelling during the ejection. Furthermore, the melt temperature was defined based on the decomposition temperature of the CFA and the processing temperature of the blends obtained by DSC measurements.

2.4. *Characterization*

For characterization, rectangular specimens from the disk samples were extracted according to Figure 3, with a thickness of 6 mm, width of 10 mm and a length of 85 mm. Before the mechanical test, all samples were pre conditioned at a temperature of 23.4 °C with a relative humidity of 46% for 24 hours. Four samples were tested for each blend and the averages and the standard deviations of the results were reported.

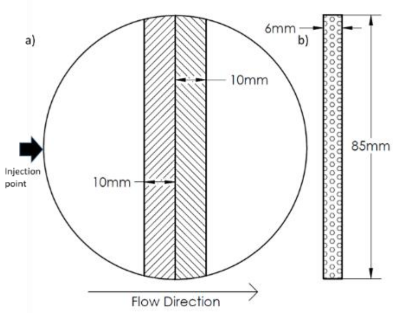

Figure 3 Scheme of the samples cut for characterization. A) Disk front view B) cross section

The density of each sample was calculated by measuring the sample weight in an analytical Mettler Toledo bb1300 and dividing by the known sample volume. Twelve samples were measured and the average values were taken for each blend.

2.4.1. Differential Scanning Calorimetry (DSC)

Thermal transitions were measured on a DSC Q200 from TA Instruments by Differential Scanning Calorimetry. The following procedure was performed to erase the thermal history and obtain the transition temperatures of the blends: 9 mg of each material were heated from 30 to 220 °C at a heating rate of 10 °C/min, using a nitrogen atmosphere (50 ml/min). Then, it was cooled down to -30°C at a cooling rate of 10°C/min, using the same atmosphere. Finally, the samples were heated again under the same conditions. The melting temperatures (Tm) and glass transition temperatures (Tg) of all the blends were reported.

2.4.2. Thermogravimetric Analysis (TGA)

TGA measurements were performed with a TA Instruments Q500 under ASTM E1131 to verify the degradation temperature and composition of the CFA. For the test, a sample of 15 mg of was heated at a heating rate of 10 °C/min from 20 to 900 °C, using a nitrogen atmosphere (50 mL/min) from 20 to 600 °C and an oxygen atmosphere (50 mL/min) from 600 to 900 °C.

2.4.3. Foam morphology Characterization

2.4.3.1. Micrographs

The cell morphology of foamed samples was studied using a Leica stereo microscope M420. The samples were previously prepared using an electric polisher to obtain a mirror finish. Micrographs at 10x magnification were obtained and analyzed with the software ImageJ V1.52n. This information was used to characterize the samples according to number of recorded cells, their size and distribution.

Furthermore, cell population density (*Cpd*) was calculated based on the Micrographs images, according to Equation 1 [20], where *n* is the number of cells in the recorded image, *A* [cm^2] is the cross section area of the sample, ρ_s is the material´s solid density and ρ_f the foamed density.

$$Cpd\ \left[\frac{Cell}{cm^3}\right] = \left(\frac{n}{A}\right)^{3/2} * \frac{\rho_s}{\rho_f} \qquad (1)$$

2.4.4. Rheological Properties.

The rheological properties of all blends were measured to analyze the complex viscosity and molecular weight variations. Tests were performed on a AR 2000 ex rotational rheometer from TA Instrument on frequency sweep mode with a parallel plate of Φ25 mm and a gap of 1.6 mm. Storage modulus (G’), loss modulus (G’’), and complex viscosity (η*) were measured as functions of frequency in the range from 600 to 1 rad/s at 200 °C.

2.4.5. Mechanical Characterization

2.4.5.1. Tensile strength

Foam strength tests were performed with a Zwick/ Roell 1455 universal testing machine. Tensile strength tests were performed under ASTMD638. The test speed was 50 mm/min with a grip to grip separation at the start position of 50 mm and 2 N of pre load, the tangent modulus were taken between a strain of 0.05 and 0.25%.

2.4.5.2. Impact strength

To analyze and compare the foamed samples toughness, notched impact strength tests were performed on a Zwick/ Roell Hit 5.5P under ASTM D256-10 1EA. The weight used was 0.17 kg with an applied impact energy of 0.116 ± 0.005 J.

3. Results and discussion

3.1. *Thermal characterization*

DSC thermograms of the first cooling show the crystallization behavior of the blends. As shown in Figure 4 a, the temperature of the peak of crystallization of PBS was increased with the presence of PLA in the blends (0DCP, 0.1DCP, 0.4CP and 1DCP), where the immiscible characteristic of the two polymer phases PLA/PBS may facilitate the nucleation process. Furthermore, according to Nofar et al.[4], crosslinked structures affect the crystallization. Without DCP (0DCP), the crystallization temperature of PBS phase in the blend is 86.85°C and with 0.1% DCP this temperature increases 9.02 °C and the onset crystallization temperature shifted to 100 °C. An increase of the crystallization temperature enhances the cell stability during cooling, avoiding their collapse and obtaining a more stable structure. Additionally, an increase of crystallinity of the PBS phase is obtained with the blend. Neat PBS reaches a crystallization enthalpy of 67.63 joules per gram of PBS. Meanwhile, the blend 0DCP reaches 49.85 joules per gram of blend. Since the blend has 60% of PBS, the adjusted crystallization enthalpy is 82.65 Joules per gram of PBS. The increase of peroxide reduces the molecular mobility, explaining the crystallization enthalpy reduction when 1% of DCP is used.

Figure 4b shows the DSC curves of neat materials and blends. The glass transition temperature (T_g) of PLA is 58 °C and the peak of melt temperature (Tm) is around 150 °C. For PBS, the melting peak is at 114 °C. For all the blends, transition temperature of PLA and PBS are not significantly modified. However, with the increase of DCP, the melting peak tends to decrease, which suggest that the molecular mobility during crystallization process is reduced, due to the high crosslinking degree of the blend.

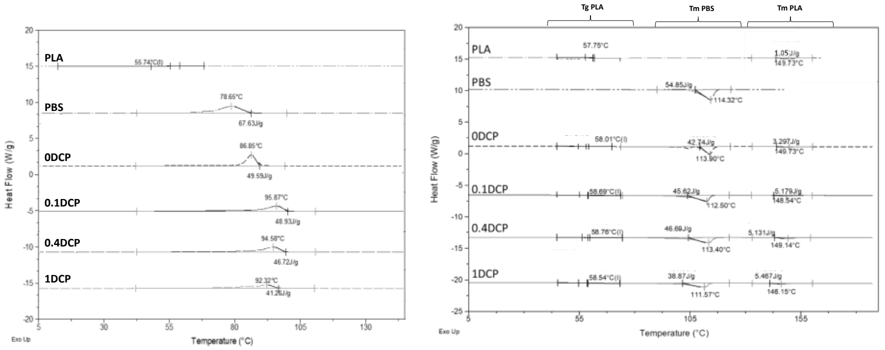

Figure 4 DSC of neat materials and blends. a) First cooling at a rate of 10°C/min b) Second heating at a rate of 10°C/min.

The TGA curve of the CFA presented in Figure 5 shows three decomposition temperatures. The onset decomposition temperature is around 190 °C and reaches its peak near 220 °C. According to Reyes-Labarta [21], the first peak represents the primary decomposition of the azodicarbonamide where hydrazodicarbonamide, cyanic acid and nitrogen gases are obtained. The peak of decomposition temperature of PE is observed around 467°C. The content of azodicarbonamide in the CFA masterbatch was confirmed (25% wt).

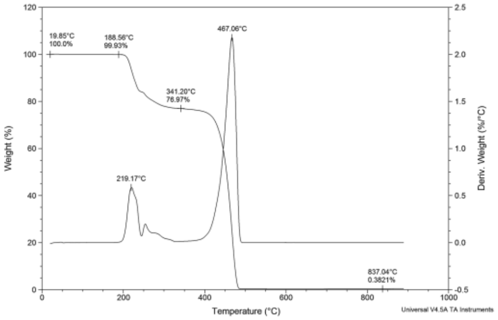

Figure 5 TGA of chemical foaming agent Arcoplast PE 2589

In chemical foaming, CFA should reach its decomposition temperature during the injection molding process, but the processing temperature should be as low as possible in order to increase the melt strength, and therefore, the cell stability. For this reason, the recommended temperature process for foam injection molding should be around 210 °C. This value is approximately 60°C above the melt temperature of PLA, allowing an adequate gas generation and mix inside the polymer matrix.

3.2. *Rheological Behavior*

High melt viscosity at a low shear rates is characteristic of materials with adequate foaming capabilities because it is related to the material melt strength. This property is required to prevent cell collapse and obtain a good foam structure [22]. Figure 6 shows the frequency dependence of the blends complex viscosity.

According to the Cox-Merz rule [23], the complex viscosity is qualitatively related to the shear viscosity, and frequency is qualitatively related to shear rate. Based on this rule, neat PLA shows a Newtonian behavior with frequencies below 10 rad/s, while PBS and all the blends have a shear thinning response in all the measured range. As expected, DCP increases the viscosity. However, the shear thinning behavior allows the blend processability at high shear rates, reaching viscosity close to those of the neat materials as was previously reported in other works [14]. The viscosity of blend 1DCP was not possible to measure due to the high crosslinking degree of the blend.

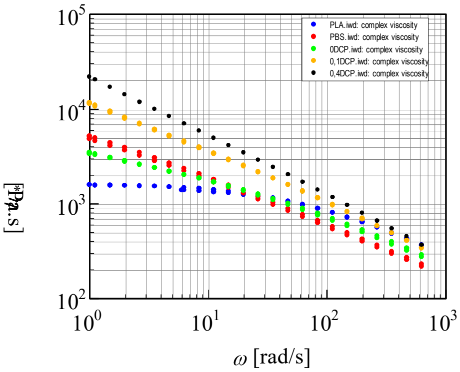

Figure 6 Frequency dependence of complex viscosity of PLA/PBS/ DCP blends.

High molecular weight (Mw) is related to a high melt strength. The storage modulus (G') is related to the elastic portion in the polymer [22]. From G' and G'' response (Figure 7), it can be concluded that the higher the DCP content, the higher Mw, and hence, its melt strength. The lower storage modulus was obtained for the PLA at low shear rates, but it equals the PBS at higher shear rates. The higher G' value is obtained when DCP is used, but there are not noteworthy changes when DCP content goes from 0.1 to 0.4 %wt.

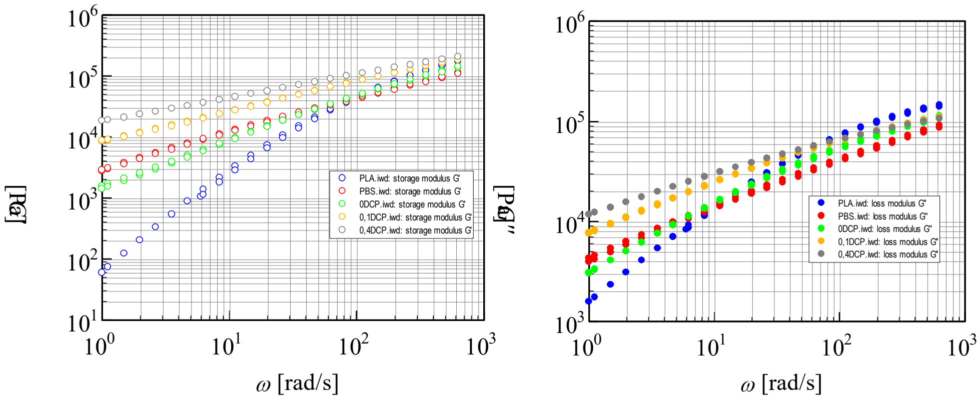

Figure 7 Storage modulus G' and loss modulus G'' of PLA/PBS/DCP blends

3.3. *Physical and morphological properties*

As expected from the rheological characterization, all the blends but 1DCP were able to form a well-shaped foamed disc samples during the foam injection process. The value of 0.4DCP was selected since higher DCP concentrations make difficult the foam injection molding process. This result disagrees with the DCP contents used in some works, where amounts of peroxide higher than 3% wt are reported for PLA and PBS foaming [19]. This difference may be explained by the use of materials with lower molecular weight.

Since all samples were injection molded under the same processing conditions, the obtained results of foamed density and expansion ratio were similar, delivering values around 0.85 ± 0.06 g/cm^3 and of 1.45 ± 0.05, respectively. Therefore, the obtained differences can be explained by the variability of the process and measurements and not by the composition of the blends.

3.3.1. Micrographs

Figure 8 shows the foamed structures of the neat polymer and blends after foaming. All samples exhibited close cell structures with two well-defined regions. The first region is a solid skin, which is the material that first touches the mold wall, cooling down without allowing the cells formation and growth. This skin is usually found in any foamed injection molding part. The second region is the foamed core. The solid layer/part thickness ratio in foamed parts is ruled by the material thermal properties and processing parameters [20], and since the last ones were fixed, the difference can only be related to the foaming capabilities of the blends. The solid layer ratios were in the range from 17 to 28 %, where the highest ratio was obtained for neat PLA. This can be explained by the material melt temperature, since the PLA temperature is 36°C higher than that of PBS (Figure 4). Therefore, PLA reaches its transition temperature faster than PBS during part cooling increasing the solid layer. The cell formation and growth in PLA is limited to the part core, resulting in a large number of small cells in that region compare to the other materials. In all cases, the incorporation of PBS reduces the solid layer thickness because PBS has a lower melt temperature, which allows the cell formation during part cooling.

As can be seen in Figure 8, the shape of cells in the PLA sample is slightly oval. Meanwhile, the morphology in the PBS and 0DCP samples tends to be circular. On the other hand, in the samples with DCP (0.1DCP and 0.4DCP), the cells are oval and highly oriented in the flow direction. In these samples, the orientation induced by the flow is maintained by the crosslinking process, obtaining and anisotropic structure.

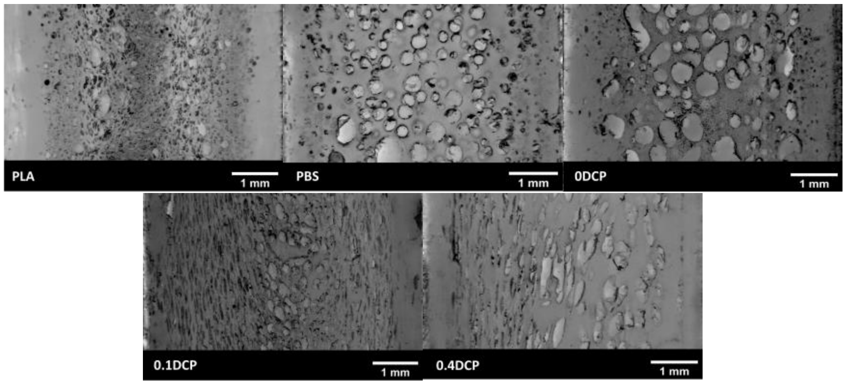

Figure 8 Micrograph images of foamed neat materials and blends at 10X magnification. A) PLA B) PBS C)0DCP D)0.1DCP E)0.4DCP

Figure 9 presents the cell population density as a function of the DCP content. The foamed neat PLA and PBS are presented as horizontal lines. The highest cell population densities and cell counts were obtained for PLA and 0.1DCP blend. In theory, the higher the cell population, the better the mechanical performance [24]. However, as will be discussed in the mechanical characterization, not only cell population is relevant but the material properties of the unfoamed blends.

The blend with 0.1% of peroxide offered a good compromise between the cell nucleation of the PLA with enhanced thermal behavior, allowing the cell formation and growth across the thickness. The blend without DCP showed the lower cell population density. This is expected due to the low compatibility between PLA and PBS that affects the cell structure stability. Blends with contents of DCP higher than 0.4% reduced the foaming capability due to the high crosslinking degree.

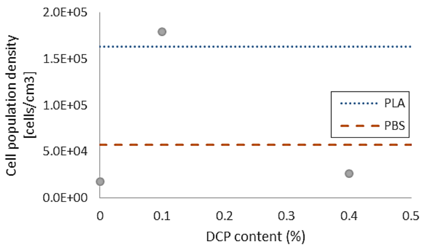

Figure 9 Cell population density of foamed samples

The cell size distributions of the samples were adjusted by a log-normal model. The results are presented in Figure 10, where “Loc” represents the average of the natural logarithm of the cell size and “Scale” its standard deviation, which is related to the width of the log-normal distribution. Neat PLA presents the smaller cell size with a “Loc” of 4.312 (equivalent to 75 µm) and the narrowest distribution with a “Scale” of 0.5983, with 50% of cells in a range from 30 to 92 µm. PBS presented an equivalent average cell size of 125.1 µm and a wider size distribution than PLA, having 50% of cells in a range of 27 to 149 µm diameter. The highest “Scale” values are obtained with 0DCP and 0.4DCP. This can be explained by the low compatibilities between the phases of the 0DCP blend and the high crosslinking of the 0.4DCP blend. High “Scale” values are not desired because this is a symptom of large cell presence, which may affect the mechanical properties. Finally, 0.1DCP offers better foaming structure morphology than the other blends, with an equivalent average cell size of 121.1 µm and a narrow cell size distribution.

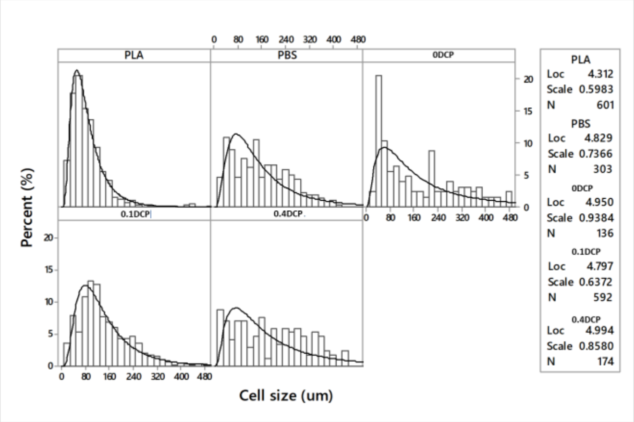

Figure 10 Cell morphology and size distribution

3.4. *Mechanical characterization*

Tensile and impact properties of blends are listed in Table 3. Results are presented as relative values dividing the material property by the foam density. E.g. yield strength/density (called relative yield strength).

Table 3 relative mechanical properties

Sample	**Relative young modulus** **(Mpa * cm^3/gr)**	**SD (+/-)**	**Relative tensile strength** **(MPa* cm^3/gr)**	**SD (+/-)**	**Elongation at break (%)**	**SD (+/-)**	**Relative impact strength** **(kJ/m^2* cm3/gr)**	**SD (+/-)**
PLA	1637.41	77.15	24.71	0.98	3.15	0.52	1.94	0.21
PBS	471.22	6.95	19.47	0.24	12.89	0.80	4.55	0.23
0DCP	747.80	45.48	16.52	0.38	3.87	0.47	2.65	0.10
0.1DCP	741.71	9.32	18.79	0.38	6.99	0.45	4.06	0.21
0.4DCP	778.73	38.22	15.11	0.53	3.84	0.24	4.17	0.19

As stated before, the main goal of adding a ductile, flexible polymer like PBS to a rigid, brittle polymer such as PLA is to improve the toughness and reduce the rigidity of the PLA. In all cases, samples failed with a brittle fracture. As expected, the highest relative Young modulus was obtained with PLA and the lowest value with PBS. All the blends reported similar modulus with a reduction of nearly 2.2 times the elastic modulus of neat PLA but around 1.5 times higher than PBS. In this property, the effect of the DCP content is negligible. The stiffness may be dominated by the solid skin of the samples; therefore, the effect of the foaming structure does not play a major role. Regarding the relative tensile strength, the best performance is obtained with PLA. The values of relative tensile strength for all the blends are slightly lower than PBS, obtaining the best performance with 0.1DCP.

Regarding the elongation at break, the best performance was obtained with neat PBS and the lowest value with PLA. The major effect of the materials incompatibility was observed in this property, where the 0DCP blend reaches a similar deformation to PLA. By adding a low content of peroxide (0.1DCP), almost twice the elongation of the uncompatibilized blend is reached. However, the elongation drops again as the DCP content is increased. Peroxide is added in order to increase the compatibility of both phases; however, large quantities generate a highly crosslinked structure, affecting the ductility of the blends. The obtained elongation at break value for 0.1DCP approximately follows the mixing rule (60% PBS, 40% PLA); therefore, a good balance of this property is obtained.

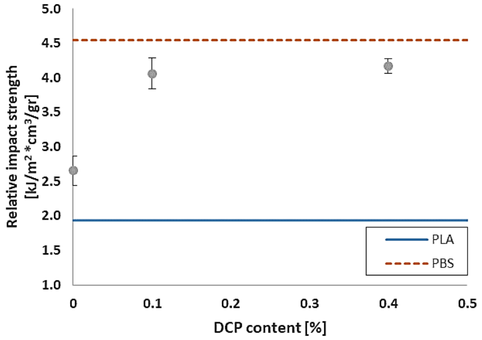

Figure 11 relative notched impact strength for foamed samples

Figure 11 presents the relative notched impact strength as a function of the DCP content. Foamed PLA and PBS results are presented as horizontal lines. The best relative impact strength was obtained with PBS with almost 2.4 times the value of the PLA. By blending PLA and PBS without a compatibilizer (0% DCP), the obtained impact strength is closer to PLA than PBS. However, by adding DCP, a stunning effect on impact strength is obtained, reaching almost the same strength of PBS. The results are similar for contents of 0.1% and 0.4% of DCP.

4. Conclusion

In this study, compounds of PBS and PLA were prepared using an industrial scale twin-screw extruder, where DCP was used as compatibilizer and foamability enhancer of the blends. The neat materials and obtained blends were foam injection molded by chemical foaming in a conventional injection molding machine with azodicarbonamide as CFA. Mechanical properties and thermal behavior were studied in order to analyze their processability and performance. Also, the morphology of the obtained foamed structures were analyzed and discussed. The blend of PLA with PBS was studied because of their complementary properties.

It was evinced that PLA/PBS blend had poor results in its foaming capabilities and mechanical performance due to phase's incompatibilities. However, the addition of DCP greatly increased the blends performance. PBS enhanced the thermal behavior of the blend, PLA the cell nucleation and the DCP increased the melt viscosity, crystallization, and materials compatibility. As a result, foamed samples of 0.85 g/cm^3 with closed cell structure and higher cell population densities than both neat materials could be obtained. Best results were achieved when 0.1%wt of DCP was used, with a good compromise of properties. The blend viscosity and melt strength were increased, its crystallization behavior enhanced, the rigidity of the foamed material was reduced by nearly 2.2 times the elastic modulus of PLA. The relative impact strength was significantly increased from 1.9 to 4.0 kJ-cm^3/m^2-g. Regarding the morphology, the obtained samples structure presented a narrow cell size distribution and a cell population density of 1.8E+05 cells/cm^3. However, high contents of DCP presented high crosslinking degrees, negatively affecting the foaming capabilities and performance of the blends. In fact, no foamed samples could be obtained when 1%wt of DCP was used.

Other chemical and physical modifications, such as the use of fillers, plasticizers, use of different PLA/PBS ratios and inclusion of new polymers in the blend, among others, are worthy to study in future works in order to enhance the mechanical performance of PLA/PBS/DCP foams.

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